Faculty of Science
Department of Chemistry

Fundamentals of

QUANTUM CHEMISTRY

Lecture notes for B.Sc. Chemistry students

2021

INTRODUCTION

Some Important Terms and Definitions:

- ***A Chemical system*** can be studies either from a macroscopic or microscopic point of view.

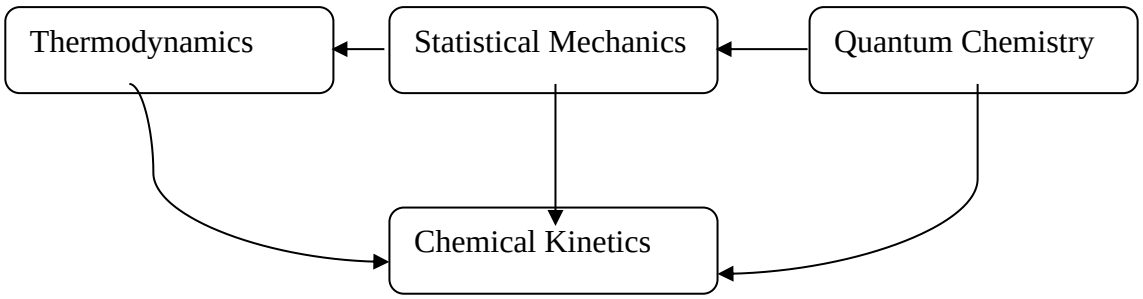
- ***The macroscopic viewpoint:*** Is based on studying the large-scale properties of matter without the use of the molecule concept.

- ***The microscopic viewpoint:*** Is based on the concept of molecules.

- ***Physical chemistry:*** It is the study of underlying physical principles that govern the properties and behaviour of chemical systems.

- ***Chemical physics:*** This term refers to the aspects of physical chemistry that study phenomena at the molecular level.

Physical chemistry is divided mainly into four areas; thermodynamics, quantum chemistry, statistical mechanics and chemical kinetics. The following diagram illustrates how these four areas relate to each other:



1. Thermodynamics:

It is a macroscopic science that studies the energy, the interrelationships of the various equilibrium properties of a system and the changes in equilibrium properties in processes.

2. Quantum Chemistry:

It applies quantum mechanics to solve problems concerning atomic structure, molecular bonding and spectroscopy.

3. Statistical Mechanics:

It gives insight into why the laws of thermodynamics hold and allows calculations of *macroscopic thermodynamics* from *molecular properties*.

So it is the bridge from microscopic approach of quantum chemistry to the macroscopic approach of thermodynamics.

In other words, the macroscopic science of thermodynamics is a consequence of what is happening at a molecular (microscopic) level.

The microscopic and macroscopic levels are related to each other by this branch of science, Statistical mechanics.

4. Chemical Kinetics:

It concerns with studying rate process such as chemical reaction, diffusion and flow charge in an electric cell.

It utilizes many basic concepts of the other three branches; thermodynamics, quantum chemistry and statistical mechanics.

The importance of physical chemistry comes from the fact that its fundamental principles provide a framework for all branches of chemistry.

The word ***Quantum*** in Latin means how much.

Quantum Chemistry is a branch of physical chemistry that applies quantum mechanics to solve problems in chemistry regarding atomic structure, molecular structure and spectroscopy. ***Quantum mechanics*** is a set of mathematical laws used to describe the behaviour of motion of microscopic systems such as electrons, protons, atoms and molecules.

Quantum chemistry deals with microscopic systems and has a statistical nature.

Some Limitations of Classical mechanics:

1. The incorrect values of heat capacities at constant volume C_V, of polyatomic molecules, as predicted by the kinetic theory of gases.
2. Its inability to explain the observed frequency distribution of radiant energy emitted by a hot solid (Black body-radiation).
3. Its inability to explain the Photoelectric effect phenomenon.

In the following, we will discuss some of the experimental phenomena that the classical mechanics (Newtonian Mechanics) have failed in explanation and how the new (quantum mechanics) succeeded.

1. BLACK BODY-RADIATION AND ENERGY QUANTIZATION

A *black body* is anybody that absorbs all the light falls on it.

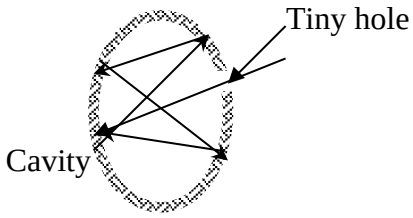


Figure 1.1: *An approximation to a black body; a cavity with a tiny hole.*

- ***Review:***

According to the classical physics, if a solid is heated, it emits light that is consisting of electromagnetic waves. The frequency ν of such wave and its wavelength λ are related together by the equation:

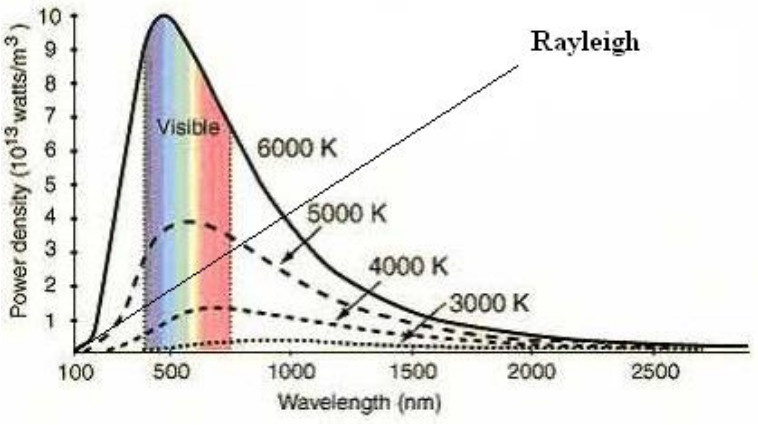
$$\nu = \frac{c}{\lambda}$$

where c is the speed of light in vacuum = 3×10^{10}cm/sec.

N.B.

At the same temperature, different solids emit radiation at different rates.

(when a metal rod is heated it emits at first red, orange yellow, white and finally blue white colour).



It is clear that, *as the absolute temperature increases*, the *maximum in R(ν),* the amount of radiant energy, *shifts to higher frequencies*.

It is clear from figure (1.1) that:

1. The radiation enters the hole is repeatedly reflected within the cavity.
2. At each reflection, a certain fraction of radiation is absorbed by the cavity walls. (The larger number of reflections causes virtually all the incident radiation to be absorbed).
3. When the cavity is heated, its walls emit light, a tiny portion of which escapes through the hole.
4. It can be shown that, *the rate of radiation* emitted per unit surface area of a blackbody *is a function* of only *its temperature* and is *independent of the material* of which the black body is made.

By using a prism to separate the various frequencies emitted by the cavity, one can measure *the amount* of black body *radiant energy* emitted in a given narrow frequency range.

How did the classical physics describe the spectrum of a black body?

Lord Rayleigh (June 1900):

He attempted to derive the theoretical expression for the function R(ν), using the equipartition-of-energy theorem, and he found that:

$$R(\nu)=\left(\frac{2\pi kT}{c^2}\right)\nu^2 \qquad (1)$$

where, k: is Boltzmann's constant= 1.38×10^{-23}J/K

c: is the speed of light = 300,000 km/s

However, this result was incorrect, since it predicts that *the amount of energy radiated would increase without limit as ν increases.*

Conclusion:

The classical physics failed to predict the spectrum of black body radiation.

Max Planck:

On Oct. 19th.1900, he discovered a formula that gave a highly accurate fit to the observed curves of black body radiation. His formula was:

$$R(\nu) = \frac{a\,\nu^3}{e^{\frac{b\,\nu}{T}} - 1}$$ *"Trial and error formula without explanation"* (2)

Where **a** and **b** are constants with certain numerical values.

On Dec. 12th.1900, he presented a theory that yielded the black body-radiation formula, which he had found empirically a few weeks earlier.

Planck's theory gave the constants **a** as $a = \frac{2\pi h}{c^2}$ and **b** as $b = \frac{h}{k}$ where *h* is Planck's constant.

Thus, the Planck's theoretical expression for the frequency distribution of black-body radiation was:

$$R(\nu) = \frac{2\pi h}{c^2} \frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1}$$ (3)

How did Planck derive this equation?

For this purpose, he introduced the hypothesis that:

> The radiating atoms or molecules of the blackbody could emit and absorb electromagnetic energy of frequency (ν) only in amounts of *h*ν, (where *h* is Planck's constant and has the dimension of energy × time).

If ΔE is the energy change in a black body *atom* due to *emission* of electromagnetic radiation of frequency ν, then:

$$\Delta E = h\nu$$

where $h = 6.626 \times 10^{-34}$ J.s

$= 6.626 \times 10^{-27}$ erg.s

This assumption leads to the above equation (3).

In **classical physics** *energy takes on a continuous range of values*, and a system can *lose* or *gain* any amount of energy.

2. PHOTOELECTRIC EFFECT

This is the phenomenon of emission of electrons from metal surfaces when an electromagnetic radiation falls on these surfaces.

A direct application of photoelectric effect is the *photoelectric cell*, which used in:

- Light intensity measurement.
- Elevator doors to prevent people crushing.
- Smoke detectors.

Some observations in photoelectric effect:

It had shown experimentally (around 1900) that:

1. Electrons were emitted only when the frequency of the light exceeds a certain minimum frequency called *threshold frequency* ν_0. (Of course, the value of ν_0 differs for different metals and lies in the UV region for most metals).
2. The number of emitted electrons was increased by increasing light intensity and not by light frequency.
3. Increasing light frequency increased the kinetic energy of the emitted electrons.

How did the classical physics fail in describing these observations?

According to the classical (wave) mechanics,

1. The energy in a wave is proportional to its intensity and is independent to its frequency. Therefore, one should expect that the kinetic energy of the emitted electrons to increase with the light intensity and not with its frequency.
2. Based on the wave picture of light, it predicted the photoelectric effect to occur at any frequency (providing that its intensity is sufficient).

How did the quantum theory succeed in describing these observations?

Einstein (1905)

1. He explained the photoelectric effect by extending Planck's concept of energy quantization to EMR.

N.B.

(*Planck had applied the energy quantization to the emission process but had considered the EMR to be a wave).*

2. He proposed that, beside the wavelike properties, light could also be considered to consist of particle-like entities called quanta, each quantum of light having an energy *hν* where ν is the frequency of light**).** these entities were later named photons, and the energy of a photon is:

$\mathbf{E}_{photon} = \mathbf{h}\nu$ (1)

Since the energy in a light beam is the sum of these energies of the individual photons therefore, it is quantized.

Let an EMR of frequencyν fall on a metal, thus:

1. The photoelectric effect occurs when an electron in the metal is hit by a photon.
2. The photon disappears, and its energy **h**ν is transferred to the electron.
3. Part of the energy absorbed by the electron is used to overcome the forces holding the electron in the metal, and the reminder part appears as a KE of the emitted electron.

Therefore, conservation of energy gives

$$h\nu = \Phi + \frac{1}{2} m \upsilon^2 \quad (2)$$

Where; **Φ** = the work function, is the minimum energy needed by an electron to escape the metal.

½ mυ² = the kinetic energy of the free electron.

N.B.

Since the valence electrons in metals have a distribution of energies, so, some electrons need more energy than others to escape the metal surface. Therefore, the emitted electrons show a distribution of kinetic energies, and **½ mυ²** in eq. (2) is the maximum kinetic energy of the emitted electrons.

How did Einstein success in describing the photoelectric effect?

Einstein's equation (2) explains all the observations in the photoelectric effect as follow:

1. If the light frequency h*ν*≤ Φ:

A photon does not have enough energy to allow an electron to escape the metal and no electric effect occurs.

The minimum frequencyν at which the effect occurs is given by h*ν*>**Φ.**

(Φdifferes for different metals, being lowest for all alkali metals).

2. Eq. (2) indicates that the KE of the emitted electrons to increase with vand to be independent of the light intensity.

An increase in *intensity* with no change in frequency increases the energy of the light beam and hence increases the number of photons per unit volume in the light beam, thereby increasing the rate of emission of electrons.

Einstein obtained a value of *h* in close agreement with Planck's value deduced from the blackbody radiation formula. This surely was a fantastic result because the whole business of energy quantization was quite mysterious and not well accepted by the scientific community of the day. Nevertheless, in two very different sets of experiments, blackbody radiation and the photoelectric effect, the very same quantization constant, *h*, had arisen naturally. Scientists realized that perhaps there was something to this
quantization business after all.

Example 1:

The speed of an electron emitted from the surface of a sample of potassium by a photon is 668 km.s^{-1}. (a) What is the kinetic energy of the ejected electron? (b) What is the wavelength of the radiation that caused photoejection of the electron? (c) What is the longest wavelength of electromagnetic radiation that could eject electrons from potassium? The work function of potassium is 2.29 eV.

Solution

(a) $E_K = \frac{1}{2}mv^2$

$$E_K = \frac{1}{2}(9.109 \times 10^{-31}\text{kg}) \times (668 \times 10^{3}\text{m.s}^{-1})^2$$

$$E_K = \frac{1}{2}(9.109 \times 10^{-31}\text{kg}) \times (668 \times 668 \times 10^{6}\text{m}^2\text{.s}^{-2})$$

$$E_K = \frac{1}{2}(9.109 \times 668 \times 668 \times 10^{-25})\ \text{kg.m}^2\text{.s}^{-2} = 2.03 \times 10^{-19}\text{J}$$

(b) The energy of the ejected electron is equal to the difference in energy of the incident radiation and the work function:

Firstly, Convert the work function from electronvolts to joules:

1eV = 1.60218 × 10^{-19}J

$$2.29\ \text{eV} \times \frac{1.602 \times 10^{-19}\text{J}}{1\ \text{eV}} = 3.67 \times 10^{-19}\text{J}$$

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

$$h\nu = \frac{1}{2}mv^2 + \Phi$$

$$h\frac{c}{\lambda} = \frac{1}{2}mv^2 + \Phi$$

$$\lambda = \frac{hc}{\frac{1}{2}mv^2 + \Phi}$$

$$\lambda = \frac{6.626 \times 10^{-34}\text{J}.s \times 3 \times 10^{8}\text{m}.\text{s}^{-1}}{2.03 \times 10^{-19}\text{J} + 3.67 \times 10^{-19}\text{J}} = \frac{1.99 \times 10^{-25}\text{J}.\text{m}}{(2.03 + 3.67) \times 10^{-19}\text{J}} = 3.49 \times 10^{-7}\text{m}$$

(c) *The longest wavelength of radiation that can eject electrons from a substance is the wavelength that results in the ejected electron having zero kinetic energy.*

$$h\nu = \frac{1}{2}mv^2 + \Phi = 0 + \Phi$$

$$h\frac{c}{\lambda} = \Phi$$

$$\lambda = \frac{6.626 \times 10^{-34}\text{J}.s \times 3 \times 10^{8}\text{m}.\text{s}^{-1}}{3.67 \times 10^{-19}\text{J}} = \frac{1.99 \times 10^{-25}\text{J}.\text{m}}{3.67 \times 10^{-19}\text{J}} = 5.42 \times 10^{-7}\text{m} = 542\ \text{nm}$$

Example 2

When lithium is irradiated with light, the kinetic energy of the ejected electrons is 2.935×10^{-19} J for λ, = 300.0 nm and 1.280×10^{-19} J for λ = 400.0 nm. Calculate (a) the Planck constant, (b) the threshold frequency, and (c) the work function of lithium from these data.

Solution

Given information:

$KE_1 = 2.935 \times 10^{-19}$ $\quad \lambda_1$, = 300.0 nm = 300×10^{-9} m

$KE_2 = 1.280 \times 10^{-19}$ J $\quad \lambda_2$ = 400.0 nm = 400×10^{-9} m

Required quantities

(a) h (b) ν_0 (c) ϕ

(a) From the relation, KE = $h\nu - h\nu_0$

We can write:

$$(KE)_1 - (KE)_2 = h(\nu_1 - \nu_2) = hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)$$

Substituting in the above equation, gives

$$2.935 \times 10^{-19}\text{J} - 1.280 \times 10^{-19}\text{J}$$

$$= h(2.998 \times 10^{8}\text{m.s}^{-1})\left(\frac{1}{300 \times 10^{-9}\text{m}} - \frac{1}{400 \times 10^{-9}\text{m}}\right)$$

$$1.655 \times 10^{-19}\text{J} = h(2.998 \times 10^{8}\text{m.s}^{-1})\left(\frac{400 \times 10^{-9}\text{m} - 300 \times 10^{-9}\text{m}}{300 \times 10^{-9}\text{m} \times 400 \times 10^{-9}\text{m}}\right)$$

$$1.655 \times 10^{-19}\text{J} = h(2.998 \times 10^{8}\text{m.s}^{-1})\left(\frac{100 \times 10^{-9}\text{m}}{1200 \times 10^{-18}\text{m}^2}\right)$$

$$1.655 \times 10^{-19}\text{J} = h(2.998 \times 10^{8}\text{m.s}^{-1})\left(\frac{1}{12 \times 10^{-9}\text{m}}\right)$$

$$1.655 \times 10^{-19}\text{J} = h(2.998 \times 10^{8}\text{m.s}^{-1})(0.083 \times 10^{9}\text{m}^{-1})$$

$$h = \frac{1.655 \times 10^{-19}\text{J}}{(2.998 \times 10^{8}\text{s}^{-1})(0.083 \times 10^{9})} = 6.625 \times 10^{-34}\text{J.s}$$

(b) $KE = h\nu - h\nu_0$

$$h\nu_0 = h\nu - KE$$

$$\nu_0 = \frac{h\nu - KE}{h} = \frac{h\nu}{h} - \frac{KE}{h} = \nu - \frac{KE}{h} = \frac{c}{\lambda} - \frac{KE}{h}$$

$$\nu_0 = \frac{2.998 \times 10^{8}\text{m.s}^{-1}}{300 \times 10^{-9}\text{m}} - \frac{2.935 \times 10^{-19}\text{J}}{6.625 \times 10^{-34}\text{J.s}}$$

$\nu_0 = 0.999 \times 10^{15}\ \text{s}^{-1} - 0.443 \times 10^{15}\text{s}^{-1}$

$\nu_0 = 0.556 \times 10^{15}\ \text{s}^{-1} = 5.56 \times 10^{15}\text{Hz}$

(c) $h\nu = KE + \Phi$

$\Phi = h\nu - KE$

$\Phi = h\frac{c}{\lambda} - KE$

$$\Phi = \frac{6.625 \times 10^{-34}\text{J.s} \times 2.998 \times 10^{8}\text{m.s}^{-1}}{300 \times 10^{-9}\text{m}} - 2.935 \times 10^{-19}\text{J}$$

$\Phi = 6.621 \times 10^{-19}\text{ J} - 2.935 \times 10^{-19}\text{J} = 3.687 \times 10^{-19}\text{J}$

$$\Phi = \frac{3.687 \times 10^{-19}\text{J}}{1.602 \times 10^{-19}\text{J}} \times 1\text{ eV} = 2.301\text{ eV}$$

N.B.
The work function is always expressed in units of electron volts (eV) where, 1eV = 1.602×10^{-19}J

Another method of solution is calculating Φ directly from:

$\Phi = h\nu_0$

Example 3: Given that the work function for sodium metal is 2.28 eV, what is the threshold frequency ν_0 for sodium?

Solution

$\Phi = h\nu_0$

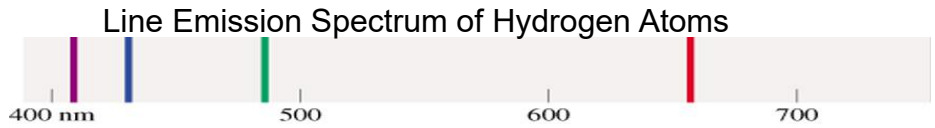
$\nu_0 = \frac{\Phi}{h}$

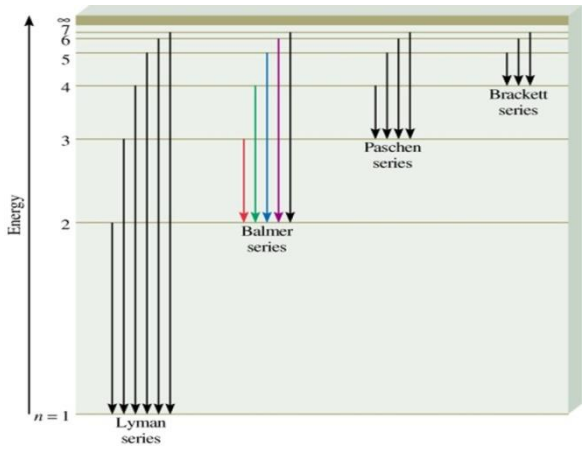
$$\nu_0 = \frac{2.28\text{ eV}}{6.625 \times 10^{-34}\text{J.s}} = \frac{2.28\text{ eV} \times 1.602 \times 10^{-19}\text{J}}{6.625 \times 10^{-34}\text{J.s} \times 1\text{eV}} = 5.51 \times 10^{14}\text{s}^{-1}$$

3. The Bohr Theory of the hydrogen atom

Another major application of the *energy quantization* is the *Bohr's theory of the H atom (1913)*.

- When a gas of H atom is heated, it emits EMR containing only certain distinct frequencies.





The various series in atomic hydrogen emission spectrum:

Series	n_f	n_i	**Spectrum region**
Lyman	1	2, 3, 4, …	Ultraviolet
Balmer	2	3, 4, 5, …	Visible and ultraviolet
Paschen	3	4, 5, 6, …	Infrared
Brackett	4	5, 6, 7, …	Infrared

- Balmer, Rydberg and others found that, the following empirical formula correctly reproduces the observed H- atom frequencies

$$\frac{\nu}{c} = \frac{1}{\lambda} = R\left(\frac{1}{n_b^2} - \frac{1}{n_a^2}\right) \qquad (1)$$

Where; $n_b = 1, 2, 3, \ldots$

$n_a = 2, 3, 4, \ldots, n_a > n_b$

R is Rydberg constant = 1.096776×10^5 cm^{-1}.

- There was no explanation for this work until Bohr's work.

Bohr said that: If one accepts Einstein's equation;

$$E_{photon} = h\,\nu,$$

The fact that only *certain frequencies of light* are emitted by H–atoms indicates that *contrary to classical ideas*, a hydrogen atom can exist only in certain energy states.

Bohr, therefore, *postulated* that:***The energy of H-atom is quantized.***

The Bohr's Postulates:

His theory based on five postulates, the first three basic postulates are called the quantization rules.

Postulate I:

An atom can take on only certain definite values of energies, E_1, E_2, E_3, …

Bohr called these *allowed states* of constant energies the *stationary states* of the atom.

N.B.

The term *stationary state does not* imply that the electron is *at rest* in a stationary state.

Postulate II:

An atom in its *stationary state does not emit* any type of electromagnetic radiation.

Postulate III:

In order to explain the line spectrum of H atom, he postulated that:

An atom when makes a transition from a stationary state with higher energy E_a to a stationary state with lower energy E_b,*it emits* a photon of light.

Since, $E_{photon} = h\,\nu$

Conservation of energy gives:

$E_a - E_b = h\,\nu$ (2)

Where,

$E_a - E_b$: the energy difference between the atomic states involved in the transition.

ν: the frequency of the light emitted.

Similarly, when an atom makes a transition from a stationary state with lower energy to a stationary state with higher energy, it absorbs a photon with frequency given by the above equation (2).

N.B.

The Bohr Theory did not provide the description of the transition process between two stationary states. "Such transitions can occur by several means such as absorption, emission of EMR and also an atom can gain or lose energy in a collision with another atom".

From equations (1) and (2);

$$E_a - E_b = R\, h\, c \left(\frac{1}{n_b^2} - \frac{1}{n_a^2} \right)$$

Such equation indicates that the energies of the H-atom stationary states are given by $E = -\frac{R\, h\, c}{n^2}$, n = 1, 2, 3, … *(the negative sign refers to the fact that we discuss a bound state of the electron)*.

Since the first three postulates are *in consistence with* the quantum theory, for this reason, the *Bohr Theory*, sometimes called, ***the old quantum theory***.

However, Bohr introduced the next two postulates to derive a *theoretical expression* for the Rydberg constant:

Postulate IV:

The electron in an H-atom stationary state moves around the nucleus in a circular orbit (path) and obeys in its movement the laws of classical mechanics.

According to the classical mechanics, the *energy* depends on the *radius* of the orbit. And since the *energy is quantized*, (in accordance with the first three postulates), *only certain orbits are allowed*.

To select the allowed orbits, Bohr introduced the following:

Postulate V:

The allowed orbits are those for which, the orbital angular momentum of electron, L ($L = m_e \upsilon r$), is an integer multiple of, $\hbar$, $\left(\hbar = \frac{h}{2\pi}\right)$.

i.e., $m_e \upsilon r = n\left(\hbar = \frac{h}{2\pi}\right)$

where; m_e: is the mass of the electron.

υ: is the speed of the electron.

r: is the radius of the orbit.

n: is the principal quantum number = 1, 2, 3, …

Another importance of this postulate is that; it introduced the*quantization of the angular momentum*.

Since the last two postulates are in consistence with the classical theory, for this reason, the Bohr theory, again, sometimes called, *the semi-classical theory.*

Limitations of the Bohr's theory:

Although Bohr's theory was very important in the development of the quantum theory, but in fact, the last two postulates are false.

This theory was superseded in 1926 by the **Schrödinger equation**, which provides a correct picture of the electronic behaviour in atoms and molecules.

The wave-nature of particles

de Broglie hypothesis

After Bohr:

Many attempts (1913-1925) have been done to apply the Bohr theory to atoms larger than Hydrogen and to molecules to describe their spectra. However, all of these attempts failed. So, it became clear that there was a basic error in the Bohr theory and his work to H atom has been considered as just an accident.

de Broglie obtained an equation for the wavelength λ to be associated with a material particle by reasoning in analogy with photons.

We have

$$E_{photon} = h\nu \qquad (1)$$

Einstein's special theory of relativity gives the photon energy as

$$E_{photon} = mc^2 \qquad (2)$$

Where, c: speed of light

m: relativistic mass of photon

- A photon has zero rest mass but photons always move at speed ***c*** in vacuum and never at rest.
- At speed ***c***, the photon has a nonzero mass ***m***.

Equating equations (1) and (2) yields:

$h\nu = mc^2$

but

$$\nu = \frac{c}{\lambda} \qquad (\lambda, \text{ is the wavelength of the light})$$

Thus

$$h\frac{c}{\lambda} = mc^2$$

or $$\frac{h}{\lambda} = mc$$

or $$\boxed{\lambda = \frac{h}{mc}} \qquad \text{for a photon} \qquad (3)$$

By analogy, de Broglie proposed that a material particle with mass *m* and speed υ would have a wavelength λ

$$\boxed{\lambda = \frac{h}{m\upsilon}} \qquad (4)$$

But since $m\upsilon = p$, where p is *the particle's momentum.* Thus equation (4) can be rewritten as

$$\boxed{\lambda = \frac{h}{P}} \quad \text{for a particle} \qquad (5)$$

Example 1: Calculate the de Broglie wavelength of:
(i) an electron moving at 1×10^6 m/s.
(ii) a macroscopic particle of mass 1.0g moving at 1.0 cm/s.

(i) The de Broglie wavelength of a particle is calculated from

$$\lambda = \frac{h}{m\upsilon}$$

$$\lambda = \frac{6.6\times10^{-34}\ J.s}{(9.1\times10^{-31}\ Kg)(1.0\times10^{6}\ m/s)} = 7\times10^{-10}\ m = 7A^0$$

This value of λ is on the order of magnitude of molecular dimension and indicates that; ***wave effects are important in electronic motions in atoms and molecules.***

(ii) The de Broglie wavelength of a particle is calculated from

$$\lambda = \frac{h}{m\upsilon}$$

$$\lambda = \frac{6.6\times10^{-34}\ \text{J.s}}{(1.0\ \text{g})(1.0\ \text{cm/s})} = 7\times10^{-27}\ \text{cm}$$

This extremely small size "value" of λ, (due to the smallness of Planck's constant, *h*, in comparison with mυ), indicates that; ***the quantum effects are unobservable for the motion of macroscopic objects.***

Example 2: Calculate the wavelength of an electron traveling at 1/1000 the speed of light. Mass of electron is 9.1×10^{-31} kg.

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.626 \times 10^{-34}\text{kg.m}^2.\text{s}^{-1}}{(9.1 \times 10^{-31})\text{kg} \times (1 \times 10^{-3} \times 3 \times 10^{8})\text{m.s}^{-1}} = \frac{6.626 \times 10^{-8}\text{m}}{9.1 \times 3} = 2.43 \times 10^{-9}\text{m}$$

$$= 2.43\text{nm}$$

Example 3: Calculate the wavelength of a rifle bullet of mass 5.0 g traveling at twice the speed of sound (the speed of sound is 331 m.s^{-1}).

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.626 \times 10^{-34}\text{kg.m}^2.\text{s}^{-1}}{5 \times 10^{-3}\text{kg.} \times 2 \times 331\text{m.s}^{-1}} = \frac{6.626 \times 10^{-31}\text{m}}{5 \times 2 \times 331} = 2.0 \times 10^{-34}\text{m}$$

Experimental confirmations of the de Broglie hypothesis:

1. Davisson and Germer (1927):

They bombarded Ni-crystals with a beam of electrons with low velocity and examined the reflected beam of electrons. The observed diffraction pattern was very similar to that obtained from X-ray diffraction experiments.

***** *This was the evidence for wave nature of the matter.*

2. D.J. Thomson:

He observed diffraction effects when electrons were passed through a thin polycrystalline sheet of metal (see figure 1.3).

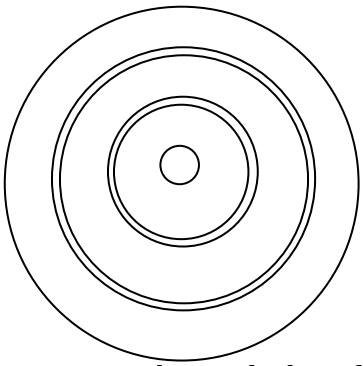


Figure (1.3): Diffraction rings observed when electrons are passed through a thin polycrystalline metal sheet.

3. Similar diffraction effects have been observed with neutrons, protons, He atoms and H_2 molecules.

Conclusion*: The de Broglie hypothesis applies not only to electrons but also to all material particles.*

Applications of the wave nature of the particles:

1. The wavelike property of electrons is used in electron microscopes. The wavelengths of the electrons can be controlled through an applied voltage, and the small de Broglie wavelengths attainable offer a more precise probe than an ordinary light microscope. In addition, in contrast to electromagnetic radiation of similar wavelengths (X rays and ultraviolet), the electron beam can be readily focused by using electric and magnetic fields, generating sharper images. Electron microscopes are used routinely in chemistry and biology to investigate atomic and molecular (crystal) structures.

2. Another important application of the de Broglie's hypothesis was a key step in our understanding of atomic structure. It can be used to give a simple, physical rationalization for the quantized Bohr orbits (first postulate). As the electron revolves around the proton (nucleus), it has wavelength λ associated with it. This situation is shown in Figure 1.4. For the orbit to be stable, it is reasonable to assume that the wave must "match," or be in phase, as the electron makes one complete revolution. Otherwise, there will be cancellation of some amplitude upon each revolution, and the wave will disappear (see Figure 1.4).

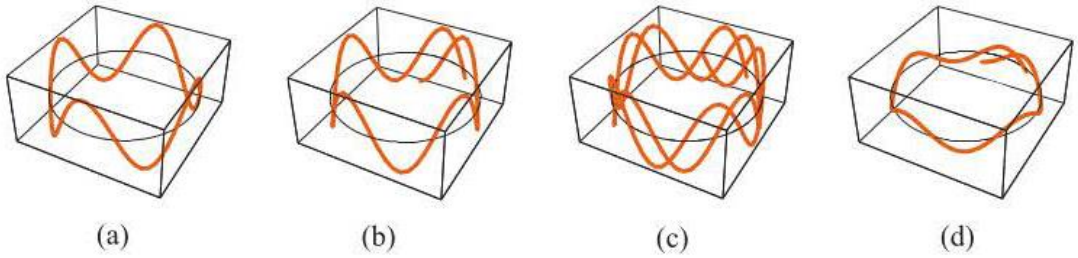


Figure 1.4: An illustration of matching and mismatching de Broglie waves traveling in Bohr orbits. If the wavelengths of the de Broglie waves are such that an integral numer of them fit around the circle, then they match after a complete revolution (a). If a wave does not match after a complete revolution (b), then cancellation will result. Slightly more than two revolutions are shown in (c), and the sum of their amplitudes is shown in (d). The wave will progressively disappear.

For the wave pattern around an orbit to be stable, we are led to the condition that an integral number of complete wavelengths must fit around the circumference of the orbit. Because the circumference of a circle is $2\pi r$, we have the *quantum condition*:

$2\pi r = n\lambda.\ n = 1, 2, 3,$ (6)

If we substitute de Broglie's relation ($\lambda = \frac{h}{p}$) into Equation 6, we obtain the Bohr quantization condition:

$$2\pi r = n\frac{h}{p} = \frac{nh}{mv}$$

which can be written as:

$$mvr = n\left(\frac{h}{2\pi}\right) = n\hbar \quad (7)$$

An interesting application of Equation (7) is to use it to calculate the velocity of an electron in a Bohr orbit.

The difference between photon and electons:

Electrons show *particle-like behaviour* in some experiments, e.g., the cathode-ray experimental and *wavelike behaviour* in others.

The wave and particle models are incompatible with each other. An entity can not be both a wave and a particle.

We can explain this apparently contradictory behaviour of electrons as follow:

The source of difficulty is the attempt to describe microscopic entities like electrons by using concepts developed from our experience in the macroscopic world.

The particle and wave concepts were developed from observations on large-scale objects, there is no guarantee that they will be fully applicable on the microscopic scale.

Under certain experimental conditions, an *electron behaves like a particle*; under other conditions, it *behaves like a wave*.

However, ***an electron is neither a particle nor a wave***.

It is something that cannot be adequately described in terms of a visualizable model.

A similar situation holds for light, which shows wave properties in some situations and particle properties in others.

Light originates in the microscopic world of atoms and molecules and cannot be fully understood in terms of models visualizable by the human mind.

Although both electrons and light exhibit an apparent wave-particle duality, there are significant differences between these entities:

Light: travels at speed c in vacuum and photons have zero rest mass.

Electrons: always travels at speed < c and have a nonzero rest mass.

THE UNCERTAINTY PRINCIPLE

Let us consider what effect the wave-particle duality has on attempts to measure simultaneously the x coordinate and the x component of linear momentum of a microscopic particle.

The discovery of wave–particle duality leads to the correct understanding of electromagnetic radiation and matter, and results in sweeps away the foundations of classical physics. In classical mechanics, a particle has a definite path (trajectory) on which location and linear momentum are specified at each instant. In quantum mechanics, however, we cannot specify the precise location of a particle if it behaves like a wave: think of a wave in a guitar string, which is spread out all along the string, not localized at a precise point. A particle with a precise linear momentum has a precise wavelength; but, because it is meaningless to speak of the location of a wave, it follows that we cannot specify the location of a particle that has a precise

linear momentum. Duality means that the electron in a hydrogen atom cannot be described as orbiting the nucleus with a definite trajectory. The popular picture of an electron in orbit around the nucleus is just plain wrong.

Wave–particle duality denies the possibility of specifying the location if the linear momentum is known, and so we cannot specify the trajectory of particles. If we know that a particle is here at one instant, we can say nothing about where it will be an instant later! The impossibility of knowing the precise position if the linear momentum is known precisely is an aspect of the complementarity of location and momentum — if one property is known the other cannot be known simultaneously.

We now know that we must consider light and matter as having the characteristics of both waves and particles. Let's consider a measurement of the position of an electron. If we wish to locate the electron within a distance Δx, then we must use a measuring device that has a spatial resolution less than Δx. One way to achieve this resolution is to use light with a wavelength on the order of $\lambda \approx \Delta x$. For the electron to be "seen," a photon must interact or collide in some way with the electron, for otherwise the photon will just pass right by and the electron will appear transparent. The photon has a momentum $p = h/\lambda$, and during the collision, some of this momentum will be transferred to the electron. The very act of locating the electron leads to a change in its momentum. If we wish to locate the electron more accurately, we must use light with a smaller wavelength. Consequently, the photons in the light beam will have greater momentum because of the relation $p = h/\lambda$. Because some of the photon's momentum must be transferred to the electron in the process of locating it, the momentum change of the electron becomes greater. A careful analysis of this process was carried out in the mid l920s by the German physicist Werner Heisenberg, who showed that it is not possible to determine exactly how much momentum is transferred to the electron. This difficulty means that if we wish to locate an electron to within a region Δx, there will be an uncertainty in the momentum of the electron. Heisenberg was able to show that if Δp is the uncertainty in the momentum of the electron, then

$$\Delta p \Delta x \geq h$$

i.e., if the location of a particle is known to within an uncertainty Δx, then the linear momentum, p, parallel to the x-axis can be known simultaneously only to within an uncertainty Δp.

Although we have analyzed only one experiment, analysis of many other experiments leads to the same conclusion: in other words, ***the product of the uncertainties in x and p_x of a particle is on the order of magnitude of Planck's constant or greater.***

However, the quantitative statement of the Heisenberg uncertainty principle is given by the relation:

$$\Delta p \Delta x \geq \frac{1}{2}\hbar$$

Where $\hbar = \frac{h}{2\pi}$

- The uncertainty principle has negligible practical consequences for macroscopic objects; owing to the small size of the Planck's constant *h*, but it is of profound importance for subatomic particles such as the electrons in atoms.
- The uncertainty principle led to a dangerous result. It turns out that the Bohr theory is inconsistent with the uncertainty principle.
- It should be noted that this uncertainty does not stem from poor measurement or experimental technique but is a fundamental property of the act of measurement itself.

The following examples demonstrate the numerical consequences of the uncertainty principle:

Example 1:
The police are monitoring a car of mass 2.0t (1t =10^3 kg) speeding along a highway. They are certain of the location of the vehicle only to within 1m. What is the minimum uncertainty in the speed of the vehicle?

Solution

m=2×10^3kg

Δx=1m

Δv=?

$$\Delta p \Delta x = \frac{1}{2}\hbar \quad \text{or} \quad \mathrm{m}\Delta v \Delta x = \frac{1}{2}\hbar$$

$$\Delta v = \frac{\hbar}{2m\Delta x} = \frac{h}{2\pi(2m\Delta x)} = \frac{6.626\times10^{-34}\mathrm{J.s}}{2\times3.14\times2\times2\times10^3\mathrm{kg}\times1\mathrm{m}} = \frac{6.626\times10^{-37}\mathrm{kg.m^2.s^{-1}}}{8\times3.14\times\mathrm{kg.m}}$$

$$= 2.63\times10^{-38}\mathrm{m.s^{-1}}$$

Example 2:

A proton is accelerated in a cyclotron to a very high speed that is known to within 3.0×10^2 km.s^{-1}. What is the minimum uncertainty in its position?

Solution

m=1.67262×10^{-27}kg

Δv= 3.0×10^2 km.s^{-1} =3.0×10^5 m.s^{-1}

Δx=?

$\Delta p \Delta x = \frac{1}{2}\hbar$ or $m\Delta v \Delta x = \frac{1}{2}\hbar$

$$\Delta x = \frac{\hbar}{2m\Delta v} = \frac{h}{2\pi(2m\Delta v)} = \frac{h}{4\pi(m\Delta v)}$$

$$= \frac{6.626 \times 10^{-34}\text{kg. m}^2\text{. s}^{-1}}{4 \times 3.14 \times 1.67262 \times 10^{-27}\text{kg} \times 3 \times 10^5\text{m. s}^{-1}} = 0.105 \times 10^{-12}\text{m}$$

Example 3:

Estimate the minimum uncertainty in:

(a) the position of a marble of mass 1.0 g given that its speed is known to within ±1.0 mm.s^{-1}.

(b) the speed of an electron confined to within the diameter of a typical atom (200. pm).

Solution

(a)

Δx=?

m= 1 g = 1×10^{-3} kg

Δv= ±1.0 mm.s^{-1} = ±1.0 $\times 10^{-3}$m.s^{-1}=2.0 $\times 10^{-3}$m.s^{-1}

$\Delta p \Delta x = \frac{1}{2}\hbar$ or $m\Delta v \Delta x = \frac{1}{2}\hbar$

$$\Delta x = \frac{\hbar}{2m\Delta v} = \frac{h}{2\pi(2m\Delta v)} = \frac{h}{4\pi(m\Delta v)}$$

$$= \frac{6.626 \times 10^{-34}\text{kg.m}^2.\text{s}^{-1}}{4 \times 3.14 \times 1 \times 10^{-3}\text{kg} \times 2 \times 10^{-3}\text{m.s}^{-1}} = 2.61 \times 10^{-29}\text{m}$$

(b)

Δv= ?

Δx= 200.pm = 200 × 10^{-12}m = 2 × 10^{-10}m

m= 9.10939×10^{-31}kg

$$\Delta v = \frac{\hbar}{2m\Delta x} = \frac{h}{2\pi(2m\Delta x)} = \frac{h}{4\pi(m\Delta x)}$$

$$= \frac{6.626 \times 10^{-34}\text{kg.m}^2.\text{s}^{-1}}{4 \times 3.14 \times 9.10939 \times 10^{-31}\text{kg} \times 2 \times 10^{-10}\text{m}} = 2.89 \times 10^{5}\text{m.s}^{-1}$$

Postulates of the quantum mechanics

Postulate 1: *"the state function"*

The ***state*** of the ***system*** is described by a function Ψ of the coordinates and the time. This function, is called ***the state function*** or wave function, and contains all the possible information that can be known about the system.

System: means either, a particle, e.g., an electron, or a group of particles, e.g., an atom or molecule.

The Concept of the State of a System

In *classical mechanics*:

The state of a system was defined by specifying all the forces, all the positions and velocities (or momentum) of the particles.

Illustrative example:

Consider the Newton's second law of motion,

$$F = ma = \frac{d^2x}{dt^2}$$

Since integration of the function ***F*** twice gives the solution of the function with two integrating constants which can be evaluated from the initial conditions.

This shows that such law allows the future state of a classical-mechanical system for a one-particle one-dimensional system to be determined from its present state.

Knowledge of the present state allows us to predict its future state with certainty.

i.e., *the classical mechanics has a deterministic nature*.

In quantum *mechanics*:

The Heisenberg uncertainty principle shown that, ***simultaneous specification of position and momentum is impossible for a microscopic particle***. Therefore, the very knowledge needed to specify the classical-mechanical state of a system is unobtainable in quantum theory. i.e., the state of a quantum-mechanical system must therefore involve less knowledge about the system than in classical-mechanics.

In quantum mechanics, the state of a system is defined by a mathematical function **Ψ** called the state function or the time-dependent wave function and the potential-energy function **V**.

The state function Ψ (origin and meaning)

Origin:

The concept of state function Ψ and its change with time were introduced in 1926 by the Austrian physicist Erwin Schrödinger.

Schrödinger was interested in the de Broglie hypothesis to search for a mathematical expression that would resemble the differential equations that govern the wave motion and that would have solutions giving the allowed energy levels of a quantum system.

Using the de Broglie relation, $\lambda = \frac{h}{p}$ and certain correct arguments, Schrödinger proposed his two equations:

1. **the time-independent Schrödinger equation:**

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2\Psi}{\partial x_1^2} + \frac{\partial^2\Psi}{\partial y_1^2} + \frac{\partial^2\Psi}{\partial z_1^2}\right) - \cdots - \frac{\hbar^2}{2m_n}\left(\frac{\partial^2\Psi}{\partial x_n^2} + \frac{\partial^2\Psi}{\partial y_n^2} + \frac{\partial^2\Psi}{\partial z_n^2}\right) + V\Psi = E\Psi$$

2. **the time-dependent Schrödinger equation:**

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2\Psi}{\partial x_1^2} + \frac{\partial^2\Psi}{\partial y_1^2} + \frac{\partial^2\Psi}{\partial z_1^2}\right) - \cdots - \frac{\hbar^2}{2m_n}\left(\frac{\partial^2\Psi}{\partial x_n^2} + \frac{\partial^2\Psi}{\partial y_n^2} + \frac{\partial^2\Psi}{\partial z_n^2}\right) + V\Psi = \frac{-h}{i}\frac{\partial\Psi}{\partial t}$$

where,

$\hbar = \frac{h}{2\pi}$, h is Planck's constant

m_1,m_n: masses of particles 1… n

x_1,y_1,z_1: spatial coordinates of particle 1

V: potential energy of the system

N.B.

1. V is derived from the forces acting on the system.
2. V is a function of the particle's coordinates, since V, potential energy is energy due to the particle's coordinates.
3. V can vary with time if an externally applied field varies with time.

The Schrödinger equation is a fundamental postulate of quantum mechanics and cannot be derived.

The reason we believe it to be true is that its predictions give excellent agreement with experimental results.

The physical meaning ofΨ:

Based on the de Broglie hypothesis, particles have wavelike properties; thus, we cannot expect them to behave like pointlike objects moving along precise trajectories. Schrödinger's replaced the precise trajectory of a particle by the wavefunction, ψ, with values that vary with position.

Schrödinger, originally, considered ψ as the amplitude of some sort of wave that was associated with the system. But his interpretation was wrong. How? A wave moving through space is a function of only spatial coordinates. Whereas, for a two-particle system, ψ is a function of the six spatial coordinates (x_1,y_1,z_1,x_2,y_2,z_2).

The German physicist **Max Born** gave the correct physical meaning of ψ "*how the wavefunction should be interpreted physically*". He postulated that "*the probability of finding the particle in a region is proportional to the value of*ψ^2.This term ψ^2 is called the *probability density*, which means, the probability that the particle will be found in a small region divided by the volume of the region.

N.B.

$$probability\ density = \frac{probability}{volume}$$

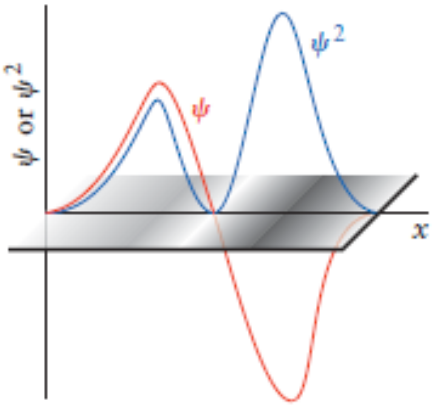


Figure: ψ^2 (the black line) is given by the square of the wavefunction and depicted by the density of shading in the band beneath. Note that the probability density is zero at a node. A node is a point where the wavefunction (the orange line) passes through zero, not merely approaches zero.

Example: If the probability density ψ^2 is 0.1 pm^{-3} at a point, calculate the probability of finding a particle in a region of volume 2 pm^3 located at that point.

Since, $probability\ density = \frac{probability}{volume}$

Thus $probability = probability\ density \times volume$

Probability= 0.1 $pm^{-3} \times$ 2 pm^3 =0.2

It is clear that larger ψ^2values means higher probability density, and vice versa.

The differences between probability and probability density:

Probability is unitless and lies between zero (uncertain) and one (certain).

Probability density has the dimensions of (volume)$^{-1}$.

Because the square of any number is positive, we don't have to worry about ψ having a negative sign in some regions of space (as a function such as sin *x* has): probability density is never negative. Wherever ψ, and hence ψ^2, is zero, the particle has zero probability density. A location where ψ passes through zero (not just reaching zero) is called a ***node*** of the wavefunction; so we can say that a particle has zero probability density wherever the wavefunction has nodes.

i.e., the physical meaning of ψ does not come from ψ itself but from the quantityψ^2.

In other words, Born postulated that, $|\Psi(x,t)|^2 dx$gives the probability at time *t* of finding the particle in the region of *x*-axis lying between *x* and *x*+*dx*. Where $|\ |$ denotes the absolute value, *dx* is an infinitesimal length of the x-axis. Therefore, the function $|\ |^2 dx$ is the probability density for finding the particle at various places on the *x*-axis.

General properties of the state functionΨ:

1. It should be well-behaved function; i.e.
   - *i.* *It must have a single valued.*
   - *ii.* *It must be continuous and finite at all points.*
   - *iii.* *It must be quadratically integrable (i.e., yields a finite value when Ψ*Ψ is integrated over all points in space).*

N.B.

"To be very well-behaved, the function and its derivatives should also be continuous functions".

2. Ψ is a function of coordinates of the particles of the system and also of time.
3. Ψ is a complex quantity.i.e., $\Psi = f + ig$

   Where, f and g are real functions of the coordinates and time.

   $i = \sqrt{-1}$.
4. The absolute value of Ψ is defined by:

$$|\Psi| = \sqrt{f^2 + g^2}$$

If g=0 thus $|\Psi| = \sqrt{f^2}$

This is the usual meaning of absolute value for a real quantity.

5. <u>The complex conjugate Ψ^* of Ψ is defined by:</u>

$\Psi^* = f - ig$ where, $\Psi = f + ig$

To get Ψ^*, replace *i* by *–i*. Thus

$$\Psi^*\Psi = (f - ig)(f + ig) = f^2 - i^2g^2 = f^2 + g^2 = |\Psi|^2$$

or $\Psi^*\Psi = |\Psi|^2$

The quantity $\Psi^*\Psi = |\Psi|^2$is both ***<u>real</u>*** and ***<u>nonnegative</u>*** as a ***<u>probability</u>*** density must be.

6. Ψ is related to physically measurable quantities.
7. Ψchanges with time.

<u>Postulate 2</u>: *Observables and operators*

Every physical ***<u>observable</u>*** is represented by a ***<u>Hermitian operator</u>***.

To find this operator, write down the classical mechanical expression for the observable in terms of Cartesian coordinates and corresponding linear-momentum components, and then replace each coordinate x by the operator $\hat{x}$ and each momentum component p_x by the operator $-i\hbar\frac{\partial}{\partial x}$.

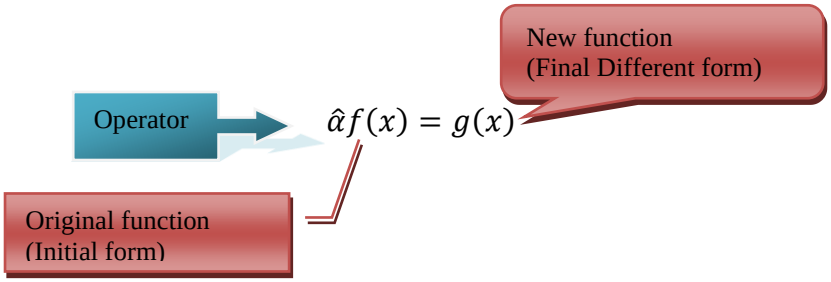
***<u>Observable</u>*:** *is any measurable dynamical variable*.

(Classical mechanics deals with quantities called dynamical variables, such as position, momentum, angular momentum, and energy).

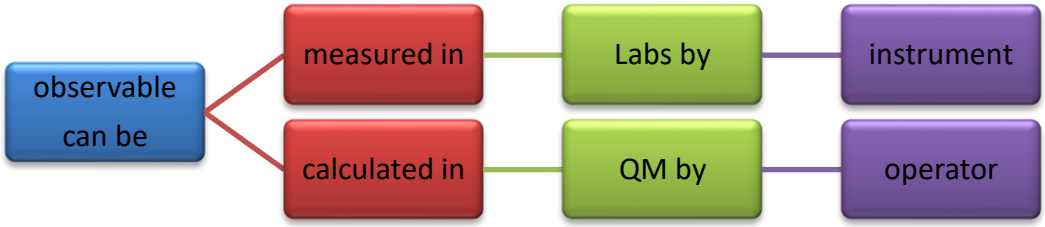
<u>Operators</u>

<u>An operator</u>: is a mathematical rule that transforms a given function into another function.

The general operator equation is



Relation between Chemistry and operators:



Every physical observable has its own operator. The name of the operator is the name of the property and it is denoted by a capital letter with a "hat" sign.

Illustrative examples

Example (1): The differential operator $\hat{d} = \frac{d}{dx}$ means "take the first derivative with respect to *x*", i.e., $\hat{d} f(x) = \frac{df}{dx}$.

If $f(x) = e^{-x^2}$

Then $\hat{d}\ f(x) = -2xe^{-x^2}$

⏭ *It is correct to say* $\hat{d}\ = -2x$

Example (2): The operator $\hat{x}$ means "multiply the function by *x*.

If $f(x) = e^{-x^2}$

Then $\hat{x}\ f(x) = xe^{-x^2}$

Example (3): The operator $\hat{C}_4$means "rotate the function by 90° about the *z*-axis". This has the effect: $x \rightarrow y$, $y \rightarrow -x$, $z \rightarrow z$ (unchanged).

If $f(x,y,z) = yx - yz + xz$

Then: $\hat{C}_4 f(x,y,z) = -xy + xz + yz$

Example (4): The inversion operator $\hat{\imath}$ means "replace *x* by –*x*, *y* by –*y*, *z* by –*z*"; that is invert the function through the origin.

If $f(x) = x^2 - 3x + 5$

Then: $\hat{\imath}\ f(x) = x^2 + 3x + 5$

Some Important operators in Quantum Chemistry

1. The Total Energy Operator or the Hamiltonian $\hat{H}$:

The most useful of the physical observable is *the total energy*; **E.** its operator is called ***the total-energy operator*** $\hat{E}$ **or the Hamiltonian** operator$\hat{\boldsymbol{H}}$.

The first step is relatively simple for the case of *velocity-independent forces* (by this restriction, we exclude for example, the case of a charged particle in a magnetic field).

***Step 1*:** write down an expression for the classical total energy of the system as a function of momentum and position "Postulate II":

The classical-mechanical Hamiltonian is:

Total energy = Kinetic Energy + Potential Energy

$H = T + V$ (1)

Where ***T*** is the **kinetic energy** which *depends on the momentum* and ***V*** is the **potential-energy function** which *depends on the coordinates*.

For a single particle of mass *m*, its kinetic energy is:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \quad (2)$$

N.B.

$$p = mv\ ; \Rightarrow v = \frac{p}{m} \Rightarrow v^2 = \frac{p^2}{m^2} \Rightarrow \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{p^2}{m^2}\right) = \frac{p^2}{2m}$$

Since the potential energy depends only on coordinates (for the case we shall consider), nothing need be done to *V* to make it an operator.

From (2) in (1):

$$E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V \qquad (3)$$

Step 2: replace each linear momentum component p_x by the operator $-i\hbar\frac{\partial}{\partial x}$ p_y by the operator $-i\hbar\frac{\partial}{\partial y}$ and p_z by the operator $-i\hbar\frac{\partial}{\partial z}$

$$\hat{E} = \hat{H} = \frac{1}{2m}\left[\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + \left(-i\hbar\frac{\partial}{\partial y}\right)^2 + \left(-i\hbar\frac{\partial}{\partial z}\right)^2\right] + \hat{V}$$

$$\hat{H} = \frac{1}{2m}\left[i^2\hbar^2\frac{\partial^2}{\partial x^2} + i^2\hbar^2\frac{\partial^2}{\partial y^2} + i^2\hbar^2\frac{\partial^2}{\partial z^2}\right] + \hat{V}$$

$$\hat{H} = \frac{1}{2m}\left[-\hbar^2\frac{\partial^2}{\partial x^2} - \hbar^2\frac{\partial^2}{\partial y^2} - \hbar^2\frac{\partial^2}{\partial z^2}\right] + \hat{V}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \hat{V}$$

The Hamiltonian operator is, then

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$$

Or

$$\hat{H} = \hat{T} + \hat{V}$$

Where $\hat{T}$ is the kinetic energy operator, and $\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$ is called the Laplacian operator (and is read as "del square").

The above equation is the starting point for all single-particle problems, and it is only the potential function that differentiates one problem from another. However, the potential function makes the difference between a simple, easy-to-solve problem and one that is very difficult.

It is clear that the Hamiltonian (or the total energy operator) $\hat{\boldsymbol{H}}$ of a microscopic particle consists of two terms. The first represents the kinetic energy operator $\hat{\boldsymbol{T}}$ and the second represents the potential energy operator ***V***. For this reason, the Hamiltonian is a considered as a compound operator.

Formulation of the Hamiltonian operator for some selected simple systems:

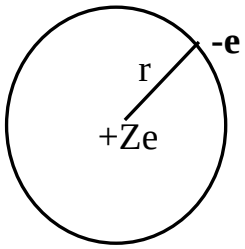
1. **H atom:**

Here we have only one electron, therefore, we have only one∇^2. So, the Kinetic energy operator becomes just one term.

And since there is only one nucleus, thus, the potential energy operator will be one term also.

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



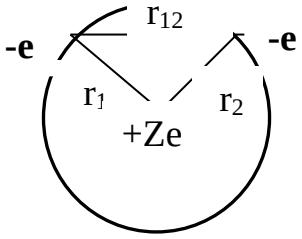
2. **He atom:**

Here we have two electrons, therefore, we have two∇^2. So, the Kinetic energy operator becomes two terms.

And since there is only one nucleus and two electrons, thus, the potential energy operator will be three terms.

$$\hat{H} = \hat{T} + \hat{V}$$

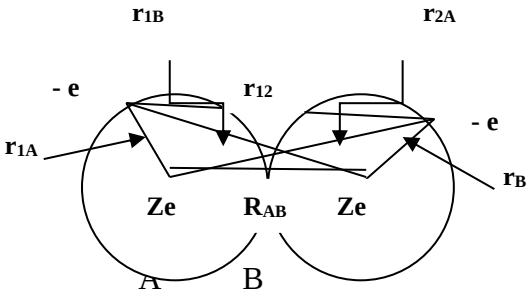
$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + \frac{e^2}{4\pi\varepsilon_0 r_{12}} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$



3. <u>Hydrogen molecule</u>:

Here we have two electrons, therefore, we have two∇^2. So, the Kinetic energy operator becomes two terms.

And since there are two nuclei and two electrons, thus, the potential energy operator will be six terms.



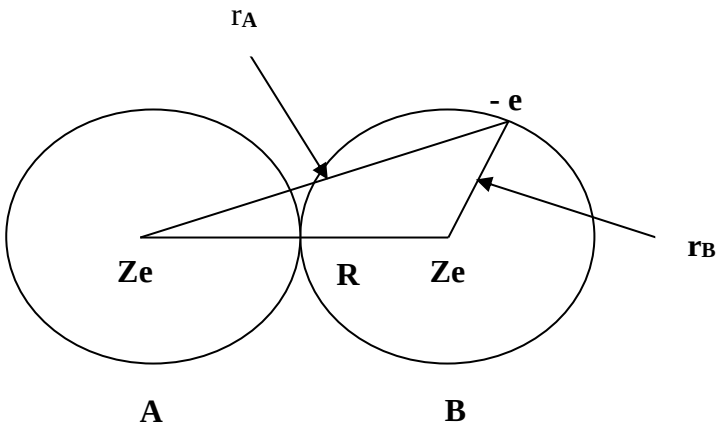
$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + \frac{z^2e^2}{4\pi\varepsilon_0 R_{AB}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} - \frac{Ze^2}{4\pi\varepsilon_0 r_{1A}} - \frac{Ze^2}{4\pi\varepsilon_0 r_{1B}} - \frac{Ze^2}{4\pi\varepsilon_0 r_{2B}} - \frac{Ze^2}{4\pi\varepsilon_0 r_{2A}}$$

4. <u>Hydrogenion molecule</u>:

Here we have one electron, therefore, we have one∇^2. So, the Kinetic energy operator becomes one term.

And since there are two nuclei and one electron, thus, the potential energy operator will be three terms.

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + \frac{Z^2e^2}{4\pi\varepsilon_0 R} - \frac{Ze^2}{4\pi\varepsilon_0 r_A} - \frac{Ze^2}{4\pi\varepsilon_0 r_B}$$



2. Angular Momentum Operator:

In QM, two kinds of angular momenta are known; the first is *Spin angular momentum* which is an intrinsic property of many microscopic particles (has no classical-mechanical analog). The second is the *Orbital angular momentum* that results from the motion of a particle through space, and is the analog of the classical-mechanical quantity ***L***.

The importance of the Angular momentum as a property comes from the fact that nearly all magnetic properties in chemistry arise from angular motion, and the energies of electrons, atoms, and molecules are often stored in some form of angular motion. The value of angular momentum lies in its being conserved in the absence of external forces, just as energy, mass, and linear momentum are. Angular momentum and all its effects result from changing the direction of motion of an object. This requires a force and involves an acceleration. That does not necessarily mean a change in kinetic energy, because circular motion at fixed speed requires a constant acceleration but no change in *V* nor in *T*.

In order to get the orbital angular momentum operator, let us follow the usual two steps (Postulate II:

Step 1: writing the classical-mechanical expression

The angular momentum operator is obtained from the cross product (vector product) of ***r*** and ***p*** vectors

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} + & - & + \\ \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\mathrm{L} = i(yp_z - zp_y) - j(xp_z - zp_x) + k(xp_y - yp_x)$$

$$\mathrm{L} = i(yp_z - zp_y) + j(zp_x - xp_z) + k(xp_y - yp_x)$$

Step 2: *replacing each momentum component into the corresponding operator*

$$\hat{\mathrm{L}} = \mathbf{i}\left(y\left(-i\hbar\frac{\partial}{\partial z}\right) - z\left(-i\hbar\frac{\partial}{\partial y}\right)\right) + \mathbf{j}\left(z\left(-i\hbar\frac{\partial}{\partial x}\right) - x\left(-i\hbar\frac{\partial}{\partial z}\right)\right) + \mathbf{k}\left(x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right)\right)$$

$$\hat{\mathrm{L}} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) - i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$\hat{\mathrm{L}} = \hat{L}_x + \hat{L}_y + \hat{L}_z$$

In the following table, there are some common operators:

Observable	**Classical-mechanical expression (vector and momentum)**	**Quantum-mechanical expression (operator)**
Position	$r = x\underline{i} + y\underline{j} + z\underline{k}$	$r = \hat{x}\underline{i} + \hat{y}\underline{j} + \hat{z}\underline{k}$
Linaer momentum	$p = p_{x\underline{i}} + p_{y\underline{j}} + p_{z\underline{k}}$ $P_x = mV_x$	$\hat{p} = \hat{p}_{x\underline{i}} + \hat{p}_{y\underline{j}} + \hat{p}_{z\underline{k}}$ $\hat{P}_x = \frac{h}{2\pi i}\left(\frac{\partial}{\partial x}\right)$ $\hat{P}_x = -i\hbar\left(\frac{\partial}{\partial x}\right)$ $-i\hbar = \frac{\hbar}{i} = \frac{h}{2\pi i}$
Angular Momentum	$L = L_{x\underline{i}} + L_{y\underline{j}} + L_{z\underline{k}}$ $L_x = mV_x r$	$\hat{L} = \hat{L}_{x\underline{i}} + \hat{L}_{y\underline{j}} + \hat{L}_{z\underline{k}}$ $\hat{L}_x = \frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$
Kinetic energy	$\frac{1}{2}mV^2 = \frac{P^2}{2m}$	$\hat{K} = \frac{P^2}{2m}$
Potential energy	$V = -\frac{Z}{r}$	$\hat{V} = -\frac{Z}{r}$

m: mass, **v**: velocity, **r**: radius, and ∇^2: del square or Laplacian operator

Linear operators:

Linear operators are a class of operators that obey the distribution law with respect to addition of functions; i.e., $\hat{\alpha}[f(x) + g(x)] = \hat{\alpha}f(x) + \hat{\alpha}g(x)$

Hermitian Operator:

Any *linear operator* $\hat{\alpha}$that satisfies the following equation, for all well-behaved functions, is said to be Hermitian:

$$\int \Psi^* \hat{\alpha}\Psi \, d\tau = \int \Psi(\hat{\alpha}\Psi)^* \, d\tau$$

Many texts define a Hermitian operator as a linear operator that satisfies:

$$\int f^* \hat{\alpha}\, g\, d\tau = \int g(\hat{\alpha} f)^* d\tau$$

As a rule, quantum-mechanical operators that represent physical quantities are required to be linear and Hermitian.

The two equations are similar

Notations

There are various abbreviations used to represent the definite integral over all space of an operator sandwiched between two functions:

1. ***Dirac notation or bracket notation*:**

   This notation was introduced by Pual Dirac (the British physicist)

   For the two arbitrary well-behaved functions f_m and f_n, the definite integrals over all space is given by

$$\int f_m^* \hat{A} f_n d\tau = \langle f_m | \hat{A} | f_n \rangle$$

The quantities $< m|$ are called *bras*, and the $|n >$ are called *kets*. This nomenclature arises from the fact that integrals such as in the above Equation is denoted by bra c kets, $\langle m|\hat{A}|n\rangle$.

2. ***matrix element notation:***

$$\int f_m^* \hat{A} f_n d\tau = \langle m|\hat{A}|n\rangle = A_{mn}$$

The notations A_{mn} and $\langle m|\hat{A}|n\rangle$ imply that we use the complex conjugate of the function whose letter appears first.

Using the bracket and matrix-element notations, we write

$$\langle f_m|\hat{A}|f_n\rangle = \langle f_n|\hat{A}|f_m\rangle^*$$

The two sides of the above Equation differ by having the functions interchanged and the complex conjugate taken.

$$\langle m|\hat{A}|n\rangle = \langle n|\hat{A}|m\rangle^*$$

$$A_{mn} = (A_{nm})^*$$

Postulate 3: *"Eigenfunction and eigenvalue"*

The measurement of a physical property observable will give a result that is one of the *eigenvalues* of the corresponding operator for that observable.

The word eigen in German means characteristic.

The Eigenvalue Equation:

The general operator equation, $\hat{\alpha} f(x) = g(x)$ has an important special case in which the new function differs from the old one only by multiplication by a constant:

$$\hat{\alpha} f(x) = a\, f(x)$$

This is called the ***eigenvalue equation***, and the constant (a) is called the ***eigenvalue***.

For a given operator, there may exist a set of functions that obey the above equation; these are called the ***eigenfunctions of the operator*****.** This set may have an infinity of members, but not all functions will be in the set (except in the trivial case that the operator is "multiplied by a constant").

Example (1): Is the function $f(x) = 7e^{-3x}$ an eigenfunction of the differential operator $\hat{d}$?

Since $\hat{d} f(x) = \frac{d}{dx}(7e^{-3x}) = -3(7e^{-3x}) = -3\, f(x)$

Thus the function $f(x) = 7e^{-3x}$ is an eigenfunction of the operator $\hat{d}$ and the eigenvalue is (-3).

Example (2): Is the function $f(x) = 7e^{-3x^2}$ an eigenfunction of the differential operator $\hat{d}$?

Since $\hat{d} f(x) = \frac{d}{dx}\left(7e^{-3x^2}\right) = -6x\left(7e^{-3x^2}\right)$. Thus the function $f(x) = 7e^{-3x^2}$ is not an eigenfunction of $\hat{d}$. This is because multiplication by *x* produces a new function. While multiplication by a constant does not produce a new function but only a change in scale. For example, the function $f(x) = 632e^{-3x}$ is an eigenfunction of $\hat{d}$ with the eigenvalue of –3.

General Rule: All functions of the form: $f(x) = ce^{kx}$ (with *k* and *c* constants) are eigenfunctions of $\hat{d}$ with eigenvalue = *k*.

Simultaneous Eigenfunctions:

Each operator has a set of eigenfunctions – *is it possible that some functions could be eigenfunctions of two different operators?*

Theorem: Two operators that do not commute may not have a complete set of functions that are eigenfunctions of both. Conversely, if the two operators do commute, such a set of simultaneous eigenfunctions will exist.

Note that*all* possible eigenfunctions of an operator need not be eigenfunctions of another, commuting operator; but some will be so.

PROOF:

Suppose that two operators $(\hat{\alpha}\ and\ \hat{\beta})$ both have some nontrivial function (ψ). (By "nontrivial" we exclude such cases as ψ= constant; normally one would not wish to consider such sets as the set of real or imaginary numbers to be functions, but some types of functions, for example e^{kx} when $k=0$, may reduce to a constant in a special case). The eigenvalue equations are:

$$\hat{\alpha}\psi = a\psi; \qquad \hat{\beta}\psi = b\psi$$

Now we operate on the first equation with $\hat{\beta}$ and on the second with$\hat{\alpha}$:

$$\hat{\beta}\hat{\alpha}\psi = ab\psi; \qquad \hat{\alpha}\hat{\beta}\psi = ba\psi$$

These two equations may be subtracted to give:

$$\hat{\alpha}\hat{\beta}\psi \ - \ \hat{\beta}\hat{\alpha}\psi = (ba \ - \ ab)\psi$$

Since a and b are numbers, ab- ba=0, and:

$$[\hat{\alpha},\ \hat{\beta}]\psi = 0 \qquad (12)$$

There are three ways in which this equation could be true:

(1) ψ =0; this can occur only as a special case – for example, *sin kx* with k =0.

(2) ψ is an eigenfunction of the commutator with eigenvalue=0; this again can occur, but only in special cases.

(3) Clearly this relationship will be true if the operators commute:

$$[\hat{\alpha},\ \hat{\beta}] = 0$$

This is the only general case for which Eq. (12) will be true – for a nontrivial set of such simultaneous eigenfunctions to exist, the operators must commute.

Example (9): Find out the result of $\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left[r^2\left(\frac{\partial}{\partial r}\ e^{ar}\right)\right]\right\}$

$$\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left[r^2\left(\frac{\partial}{\partial r}\ e^{ar}\right)\right]\right\} = \frac{1}{r^2}\left[\frac{\partial}{\partial r}(\ ar^2e^{ar})\right]$$

$$= \frac{1}{r^2}\ (2are^{ar}\ +\ a^2r^2e^{ar})$$

$$= \left(\frac{2a}{r}\ +\ a^2\right)\ e^{ar}$$

It is clear that this is not an eigenvalue equation. Why?

Example (10): The operator $\hat{h}$ has an eigenfunction, $f(x) = e^{-x^2/2}$. What is the eigenvalue?

$$\hat{h}\ e^{-x^2/2} = \left(x^2\ -\ \hat{d}^2\right)\ e^{-x^2/2} = x^2e^{-x^2/2} - \frac{d}{dx}\left(\frac{d}{dx}\ e^{-x^2/2}\right)$$

$$= x^2e^{-x^2/2} + \frac{d}{dx}\left(x\ e^{-x^2/2}\right) = x^2e^{-x^2/2} + e^{-x^2/2} - x^2e^{-x^2/2}$$

$$= e^{-x^2/2}$$

Therefore, the eigenvalue = +1.

Exercise1: Show that the function $f(x) = x\ e^{-x^2/2}$ is an eigenfunction of $\hat{h}$ with eigenvalue =3.

Exercise2: Show that the function e^{-x^2} is not an eigenfunction of $\hat{h}$.

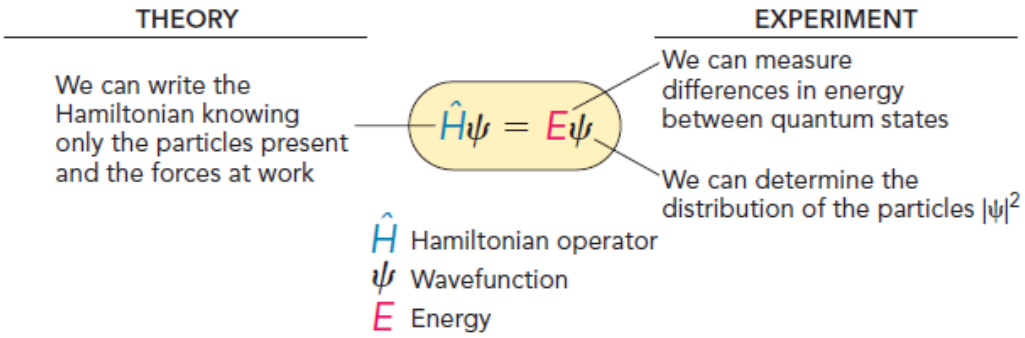
One of the most important example of the eigenvalue equation is the Schrodinger equation is an eigenvalue equation, where

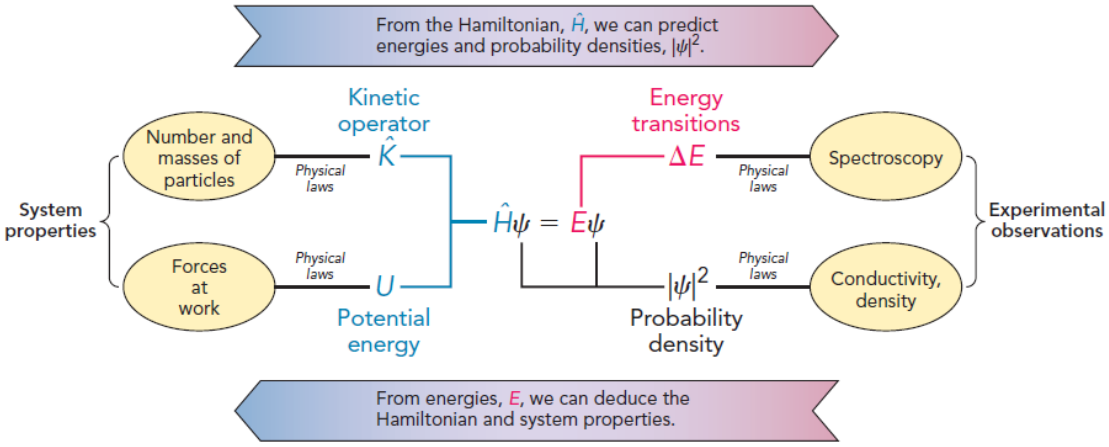
$$\hat{H}\psi = E\psi$$

$\hat{H}$ is the Hamiltomian operator.

ψ is the wavefunction or (eigenfunction)

E is the allowed total energies or (egienvalue)





1. Parity Operator$\hat{\Pi}$

The parity operator $\hat{\Pi}$ replaces each Cartesian coordinate with its negative and is defined in terms of its effect on an arbitrary function *f*:

$$\hat{\Pi} f(x, y, z) = f(-x, -y, -z)$$

This operator has no classical analog.

As a rule, with any quantum-mechanical operator, *we are interested in the **eigenvalues** c_i and the **eigenfunctions** g_i of the parity operator*:

$$\hat{\Pi} g_i = c_i g_i \qquad (1)$$

The key to the problem is to calculate the square of$\hat{\Pi}$:

$$\hat{\Pi}^2 f(x,y,z) = \hat{\Pi}\left[\hat{\Pi} f(x,y,z)\right] = \hat{\Pi}[f(-x,-y,-z)] = f(x,y,z)$$

Since *f* is arbitrary, we conclude that $\hat{\Pi}^2$ equals *the unit operator*:

$$\hat{\Pi}^2 = \hat{1} \qquad (2)$$

"The operator $\hat{1}$ (multiplication by 1) is the unit operator."

We now operate on (1) with$\hat{\Pi}$:

$$\hat{\Pi}\hat{\Pi} g_i = \hat{\Pi} c_i g_i$$

Since $\hat{\Pi}$is linear, thus,

$$\hat{\Pi}^2 g_i = c_i \hat{\Pi} g_i$$

$$\hat{\Pi}^2 g_i = c_i^2 g_i \qquad (3)$$

From (2) in (3); since $\hat{\Pi}^2$ is the unit operator, the left hand side of (3) is simply g_i, and we have

$$\hat{1} g_i = c_i^2 g_i$$

$$g_i = c_i^2 g_i \qquad (4)$$

The function g_i cannot be zero everywhere (*zero is always rejected as an eigenfunction on physical grounds*). We can therefore divide by g_i to get:

$$c_i = \pm 1 \qquad (5)$$

i.e., the eigenvalues of $\hat{\Pi}$ are +1 and -1.

Note that this derivation applies to any operator whose square is the unit operator.

What are the eigenfunctions g_i? The eigenvalue equation (1) reads

$$\hat{\Pi} g_i(x,y,z) = \pm g_i(x,y,z)$$

$$g_i(-x,-y,-z) = \pm g_i(x,y,z)$$

Thus, we have two cases:

1. *If the eigenvalue is* +1, then

$g_i(-x,-y,-z) = g_i(x,y,z)$

and g_i is an ***even function***.

2. *If the eigenvalue is* -1, then

$g_i(-x,-y,-z) = -g_i(x,y,z)$

and g_i is ***odd function***.

Conclusion: *the eigenfunctions of the parity operator* $\hat{\boldsymbol{\Pi}}$ *are all possible well-behaved even and odd functions*.

A function that is either even or odd is said to be of ***definite parity.***

2. The exchange or permutation operator $\hat{P}_{12}$

Definition: It is the operator that interchanges all the coordinates of particles 1 and 2: $\hat{P}_{12} f(q_1, q_2, q_3, \dots, q_n) = f(q_2, q_1, q_3, \dots, q_n)$

Example, find the effect of $\hat{P}_{12}$ on the function that has electron 1 in a 1*s* orbital with spin up and electron 2 in a 3*s* orbital with spin down.

$$\hat{P}_{12}[1s(1)\alpha(1)3s(2)\beta(2)] = 1s(2)\alpha(2)3s(1)\beta(1)$$

Again, in Q.M. we are interested in the eigenvalues and eigenfunctions.

What are the eigenvalues of $\hat{P}_{12}$?

$$\hat{P}_{12}\hat{P}_{12} f(q_1, q_2, q_3, \dots, q_n) = \hat{P}_{12} f(q_2, q_1, q_3, \dots, q_n) = f(q_1, q_2, q_3, \dots, q_n)$$

i.e., *Applying* $\hat{P}_{12}$ *twice has no net effect.* Therefore,

$$\hat{P}_{12}^2 = \hat{1} \qquad (1)$$

Let w_i and c_i denote the *eigenfunctions* and *eigenvalues* of $\hat{P}_{12}$. We have

$$\hat{P}_{12} w_i = c_i w_i \qquad (2)$$

Application of $\hat{P}_{12}$ to this equation gives

$$\hat{P}_{12}(\hat{P}_{12} w_i) = \hat{P}_{12}(c_i w_i)$$

$$\hat{P}_{12}^2 w_i = c_i \hat{P}_{12} w_i \qquad (3)$$

From (1), in the LHS and from (2), in the RHS of (3), we have

$$w_i = c_i^2 w_i$$

Since zero is not allowed as an eigenfunction, we can divide by w_i to get:

$$1 = c_i^2$$

$$c_i = \pm 1 \qquad (4)$$

The eigenvalues of $\hat{P}_{12}$ (*and of any linear operator whose square is the unit operator*) are + 1 and -1.

Thus, we have two cases:

1. ***If w_+ is an eigenfunction of $\hat{P}_{12}$ with eigenvalue +1, then***

$$\hat{P}_{12} w_+(q_1, q_2, \dots, q_n) = (+1) w_+(q_1, q_2, \dots, q_n)$$

$$w_+(q_2, q_1, \dots, q_n) = w_+(q_1, q_2, \dots, q_n) \qquad (5)$$

A function such as w_+ that has the property (5) of being unchanged when particles 1and 2 are interchanged is said to be ***symmetric*** with respect to interchange of particles 1 and 2.

2. **For eigenvalue -1, we have:**

$$w_-(q_2, q_1, \dots, q_n) = -w_-(q_1, q_2, \dots, q_n) \qquad (6)$$

The function w_- in (6) is ***antisymmetric*** with respect to interchange of particles 1 and 2, meaning that this interchange multiplies w_- by -1.

N.B.

Do not confuse the property of being *symmetric* or *antisymmetric* with respect to particle interchange with the property of being *even* or *odd* with respect to inversion in space.

The operator $\hat{P}_{ik}$ is defined by:

$$\hat{P}_{ik} f(q_1, \dots, q_i, \dots, q_k, \dots, q_n) = f(q_1, \dots, q_k, \dots, q_i, \dots, q_n)$$

The eigenvalues of $\hat{P}_{ik}$ are, like those of $\hat{P}_{12}$, +1 and -1.

Postulate 4: *"Expansion of superposition principle"*

If $\hat{\boldsymbol{\beta}}$ is any *linear Hermitian operator* that represents a physically observable property, then the eigenfunction g_i of $\hat{\boldsymbol{\beta}}$ forms a *complete set*.

Linear operators are a class of operators that obey the distribution law with respect to addition of functions; i.e., $\hat{\alpha}\big(f(x)+g(x)\big)=\hat{\alpha}f(x)+\hat{\alpha}g(x)$

A complete set of functions means that an arbitrary function (ψ) can be expanded exactly as a linear combination of these functions,

$$\psi(x)=\sum_n c_n\varphi_n(x) \qquad (3)$$

where c_n are constants. This is called the **superposition principle**. The concept of expansion in complete sets has wide application outside quantum mechanics. For example, the set $\{x^n\}$ for n= 0, 2, …, ∞ is a complete set, and Eq. (3) for this case is called the power series. This set is not, however, an orthogonal set. The sets of functions {sin ($n\pi x$)} or { cos ($n\pi x$)} for for$n$= 0, 1, 2, …, ∞ are both complete and orthogonal.

Postulate 5:

If Ψ(r,t) is the *normalized state function* of a system at time t, then the *average value* of a physical observable B at time t is $\langle\hat{\boldsymbol{B}}\rangle=\int\boldsymbol{\psi}^*\hat{\boldsymbol{B}}\boldsymbol{\psi}\,\boldsymbol{d\tau}$.

The Average-Value Theorem:

If the state function Ψ is an eigenfunction of a particular operator, then a measurement of the corresponding physical property will give, as an answer, the eigenvalue. If the state function (ψ) is not an eigenfunction of a particular operator ($\hat{\alpha}$), measurement will give ***one*** of the eigenvalues of that operator, but we cannot predict which one. The **average value** that will be obtained from repeated measurements can be calculated; this quantity is denoted$\langle\hat{\alpha}\rangle$, also called the **expectation value**, and is calculated by:

$$\langle\hat{\boldsymbol{\alpha}}\rangle=\int\boldsymbol{\psi}^*(\hat{\boldsymbol{\alpha}}\boldsymbol{\psi})\,\boldsymbol{d\tau} \qquad (1)$$

The integral is over "all space" as defined by the problem at hand, and we assume that ψ is ***normalized***.

In general, to calculate the average value of some physical observable in a state characterized by ψ you must

1. operate on $\psi$with the appropriate operator,
2. multiply by the complex conjugate ψ^* and
3. integrate.

But what if ψ is an eigenfunction (presumed to be normalized) of the operator? Then:

$\because \hat{\alpha}\psi = a\psi$ (2)

and $\langle \hat{\alpha} \rangle = \int \psi^* (\hat{\alpha}\psi)\, d\tau$ (3)

from (2) in (3)

$\langle \hat{\alpha} \rangle = \int \psi^* (\hat{\alpha}\psi)\, d\tau = a \int \psi^* \psi d\tau = a$

In other words, in this situation, the average value is just the eigenvalue.

There are, thus, two possibilities:

(1) The *wave function of the system is an eigenfunction of the operator*: in this case, every measurement will give the same result –the eigenvalue- which is, consequently, the average value.

(2) *The wave function is not an eigenfunction of the operator*: in this case each measurement may give a different value, whose average is given by Eq. (1).

For example, consider the average value of the radius of the hydrogen atom (as a quantum mechanical system). Consider, for simplification, a collection of only four hydrogen atoms.

H(1) H(2) H(3) H(4)

The average value of the radius is

$$r_{av} = \frac{r_1\Psi_1^2 + r_2\Psi_2^2 + r_3\Psi_3^2 + r_4\Psi_4^2}{\Psi_1^2 + \Psi_2^2 + \Psi_3^2 + \Psi_4^2} = \frac{\sum_{i=1}^{4} r_i\Psi_i^2}{\sum_{i=1}^{4} \Psi_i^2} = \frac{\int \Psi^* r \Psi \partial\tau}{\int \Psi^* \Psi \partial\tau} = \int \Psi^* r \Psi \partial\tau$$

Normalization Condition:

Normalized wavefunctions, are those wavefunctions multiplied by the proper coefficient (constant) such that the probability density over all space equals one. In other words, if we look everywhere, we must have one chance in one (i.e., a 100% chance) of finding the particle described by that wavefunction.

Normalizing the wavefunction removes any confusion as to the magnitude of ψ .

Because the Hamiltonian operator is a linear operator, if ψ is a solution to $\hat{H}\psi = E\psi$, then any constant, say, *N*, times ψ is also a solution, and *N* can always be chosen to produce a normalized solution to the Schrödinger equation, $\hat{H}\psi = E\psi$.

As mentioned before, there is a proportionality between probability and$|\psi|^2 d\tau$. In order to determine the actual value of the probability we write $\psi` = N\psi$, where N is a (real) constant selected so that $|\psi`|^2 d\tau$ is equal to the probability that the particle is in the volume element dτ. To determine this constant, we note that the total probability of finding the particle anywhere in space must be 1 (it must be somewhere).

From now on, unless we state otherwise, we always use wavefunctions that have been normalized to 1. That is, from now on we assume that ψ already includes a factor that ensures that (in one dimension).

1. *If the system is one-dimensional*, the total probability of finding the particle is the sum (integral) of all the infinitesimal contributions$|\psi`|^2 d\tau$, and we can write

$$\int_{-\infty}^{\infty} (\psi`)^* \psi` \, dx = 1$$

or

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

2. *In three dimensions, the wavefunction is normalized if*

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* \psi dx \, dy \, dz = 1$$

3. *The normalization of n-particles three-dimensional system is*:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi|^2 \, dx_1 dy_1 dz_1 \, \dots dx_n dy_n dz_n = 1$$

In general, the normalization condition may be written:

$\int \psi^* \psi \, d\tau = 1$

where dτ stands for the volume element in the appropriate number of dimensions and the limits of integrations are not written explicitly. In all such integrals, the integration is over all the space accessible to the particle.

The form of this integral is often simplified even further by using Dirac notation (replacing ψ byψ_n):

$$\langle n|n\rangle = 1$$

This Dirac bracket notation is much more succinct than writing out the integrals in full. It also introduces the words 'bra' and 'ket' into the language of quantum mechanics. Thus, the bra ⟨n| corresponds to ψ_n^* and the ket |n⟩ corresponds to the wavefunction ψ_n. When the bra and ket are put together as in the above expressions, integration over all space is understood.

Orthogonality And Completeness:

The type of operator that can represent physical variable is called a **Hermitian operator**. The eigenfunctions of a Hermitian operator have an important property: they form a complete orthogonal set.

Two functions, ϕ_n and ϕ_m, are ***orthogonal*** if the integral of the complex conjugate of one times the other is zero:

$$\int \phi_n^* \phi_m \, d\tau = 0$$

Example: Are the functions $sin(\varphi)$ and $cos(\varphi)$, defined for the interval $0 < \varphi < 2\pi$, orthogonal to each other or not?

$$\int_0^{2\pi} sin(\varphi)\, cos(\varphi)\, d\varphi = -\frac{cos^2\varphi}{2}\Big]_0^{2\pi} = -\frac{1}{2} + \frac{1}{2} = 0$$

As we have seen, these functions can be normalized, so this integral, for *n* = *m*, is equal to **1**. The combination is called **orthonormal set**:

$$\int \phi_n^* \phi_m \, d\tau = \begin{cases} 1 \text{ if } n = m \\ 0 \text{ if } n \neq m \end{cases} \qquad (2)$$

Postulate 6: *"time development"*

The time development of the state of an undisturbed quantum-mechanical system is given by the Schrödinger time-dependent equation: $-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = \hat{H}\Psi$. Where $\hat{H}$ is the Hamiltonian operator (total energy operator) of the system.

Algebraic rules for operators:

1. Equality:

The two operators $\hat{\alpha}$ and $\hat{\beta}$ are said to be equal, ($\hat{\alpha} = \hat{\beta}$), if and only if they have the same effect (result) when operated on any function. i.e.,

$\left.\begin{matrix}\hat{\alpha}f(x) = g(x) \\ \hat{\beta}f(x) = g(x)\end{matrix}\right\}$ the same new function.

2. Addition:

When the two operators $\hat{\alpha}$ and $\hat{\beta}$ operated on a function *f*(*x*) so,

$\hat{\alpha}\ f(x) = g(x)$ and $\hat{\beta}\ f(x) = h(x)$

where *g*(*x*) and *h*(*x*) are new functions, then:

$$\left(\hat{\alpha} + \hat{\beta}\right) f(x) = \hat{\alpha}f(x) + \hat{\beta}\ f(x) = g + h$$

i.e., the distributive law is obeyed.

3. Multiplication:

The symbol $\hat{\alpha}\hat{\beta}$ means operate first with $\hat{\beta}$ and then, on the result, with $\hat{\alpha}$, (i.e., *from light to left*). The operator $\hat{\alpha}^2$ means operate twice with $\hat{\alpha}$.

Example (5): Find $\hat{d}^2 f(x)$ for $f(x) = sin3x$.

$$\hat{d}(sin3x) = 3\ cos3x$$

$$\hat{d}(3\ cos3x) = -9\ sin3x$$

i.e., $\hat{d}^2(\ sin3x) = -9\ sin3x$

N.B. In many cases, operators do not necessarily commute i.e., $\hat{\alpha}\hat{\beta} \neq \hat{\beta}\hat{\alpha}$

Example (6): What is the result of operating $\hat{x}$ and $\hat{d}$ on the function $f(x) = e^{-x^2}$

⏭ If we operate firstly $\hat{d}$, we have:

$$\hat{x}\hat{d}f(x) = x\left(-2xe^{-x^2}\right) = -2x^2e^{-x^2}$$

⏭ While if we operate firstly $\hat{x}$, we have:

$$\hat{d}\hat{x}f(x) = \frac{d}{dx}\left(xe^{-x^2}\right) = -2x^2e^{-x^2} + e^{-x^2} = (1 - 2x^2)\ e^{-x^2}$$

It is clear that the two results are completely different.

4. Division:

Division is not defined for operators, except in the following sense: if $\hat{\alpha}f(x) = g(x)$, there may some operators $\left(\hat{\beta}\right)$ that reverse this transformation so that $\hat{\beta}g(x) = f(x)$. In such a case we may state:

$\hat{\beta} = \hat{\alpha}^{-1}$ or $\hat{\alpha}\hat{\beta} = 1$ meaning that $\hat{\beta}$ is the inverse operation to $\hat{\alpha}$.

Example (7): Is the inversion operator $\hat{\imath}$ is its own inverse?

Since $\hat{\imath}f(x) = f(-x)$, then $\hat{\imath}f(-x) = f(x)$. Therefore, $\hat{\imath}^2f(x) = f(x); \hat{\imath}^2 = 1$. The last is an operator equality meaning that $\hat{\imath}^2$ can be replaced by 1, the operator that means "multiply by one".

5. Commutators:

The rules or algebra apply to linear operators except for *division and the commutation rule for multiplication*. The fact that certain operators do not commute has important consequences, which we shall explore now. It will be necessary to define an operator:

$$\hat{C} = \hat{\alpha}\hat{\beta}\ -\ \hat{\beta}\hat{\alpha}$$

This operator is called the ***commutator*** and is usually symbolized as:

$$[\hat{\alpha},\ \hat{\beta}] \equiv \hat{\alpha}\hat{\beta}\ -\ \hat{\beta}\hat{\alpha}$$

⏭ The physical meaning of commutator operator is that, for any function *f*(*x*), the operation:

$$(\hat{\alpha}\hat{\beta}\ -\ \hat{\beta}\hat{\alpha})\ f(x) = \hat{\alpha}\left(\hat{\beta}\ f(x)\right) -\ \hat{\beta}\left(\hat{\alpha}\ f(x)\right) = g(x)$$

can be replaced by an operation:

$$\hat{C}\ f(x) = g(x)$$

where $\hat{C}$ is called the commutator. Operators that commute have a commutator of zero: $\hat{C}\ = 0$.

Example (8): Find the result of $[\hat{d},\ \hat{x}]$ operating on a general function *f*(*x*)

$$[\hat{d},\ \hat{x}]\ f(x) =\ \hat{d}\hat{x}f(x)\ -\ \hat{x}\hat{d}f(x)$$

$$=\ \frac{d}{dx}\left(xf(x)\right)\ -\ x\frac{df(x)}{dx}$$

Applying the partial differentiation of a product, we find:

$$\frac{d}{dx}(xf) = x\frac{df}{dx}\ +\ f\frac{dx}{dx} = x\frac{df}{dx}\ +\ f$$

$$[\hat{d},\ \hat{x}]f(x) = x\frac{df}{dx}\ +\ f -\ x\frac{df}{dx}\ = f(x)$$

Therefore,

$$[\hat{d},\ \hat{x}] = 1$$

$$\left[\frac{d}{dx},\ x\right] = 1$$

⏭ The right-hand side of the above equation is the ***trivial operator*** "multiply by the number 1".

Exercise: Prove that $[\hat{d}^2,\ \hat{x}] = 2\hat{d}$

Some Applications of the Time-Independent Schrödinger Equation

1. The particle in a one-dimensional box

or "the Particle in a Square Well"

✸**Physical Meaning:**

A particle, of mass (*m*), is subjected to a potential-energy function that is infinite everywhere along the *x*-axis except for a line segment of length *l*, where the potential – energy *V*(x) is zero. i.e.,

$$V_x = \begin{cases} 0 \text{ for } 0 < x < l \\ \infty \text{ for } l \leq x \leq 0 \end{cases}$$

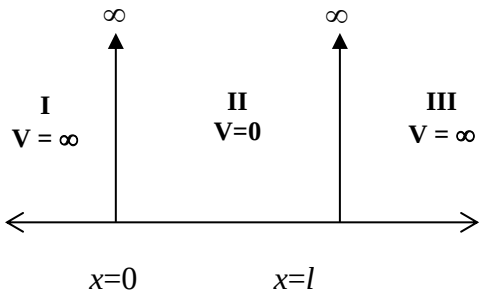


Fig. (3.1): The problem of a particle in a one-dimensional box and its potential-energy function *V*(x).

Our task is to find ψ in the three regions; I, II, and III, or inside and outside the box. i.e., solving the Schrödinger equation; $\hat{H}\psi = E\psi$ that is an eigenvalue equation.

1. outside the box: *(Regions I and III)*

The first step in solution begins with writing the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x) \qquad (1)$$

In regions (I) and (III); V = ∞ (2)

From (2) in (1)

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \infty \qquad (3)$$

the simplest form of the time-independent Schrödinger equation is

$$\hat{H}\psi = E\psi \qquad (4)$$

Substituting from (3) in (4):

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \infty\right]\psi = E\psi \qquad (5)$$

the Laplacian operator in one-dimensional is:

$$\nabla^2 = \frac{\partial^2}{\partial x^2}$$

which again can be written as ordinary differential equation as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} = \frac{d^2}{dx^2} \qquad (6)$$

From (6) in (5):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \infty\psi = E\psi$$

or

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi - \infty\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E - \infty)\psi \qquad (7)$$

Since $\infty \gg E$, thus equation (3) becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \infty\psi$$

or

$$\frac{d^2\psi}{dx^2} = \infty\left(\frac{2m}{\hbar^2}\right)\psi$$

$$\frac{d^2\psi}{dx^2} = \infty\psi$$

$$\psi = \frac{1}{\infty}\left(\frac{d^2\psi}{dx^2}\right) = 0$$

✸**Conclusions:**

1. ψ is zero outside the box. i.e., $\psi_I = 0$ and $\psi_{III} = 0$

2. $|\Psi|^2 = 0$.

Which means that the probability of finding the particle outside the box (regions I and III) is zero.

2. <u>inside the box</u>:

The same procedure is repeated; first write down the Hamiltonian taking in consideration the value of potential energy function, and then substitute in the simplest form of the time-independent Schrödinger equation:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x) \qquad (1)$$

Inside the box; "regions (II)"; at $0 < x < l$,

$$V(x) = 0 \qquad (2)$$

From (2) in (1)

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + 0 = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad (3)$$

Substituting in the Schrödinger equation:

$$\hat{H}\psi = E\psi \qquad (4)$$

From (3) in (4);

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\left(-\frac{2m}{\hbar^2}\right)\left(-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\right) = \left(-\frac{2m}{\hbar^2}\right)E\psi$$

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

or

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad (5)$$

Equation (3) is a typical ***linear homogeneous second-order differential equation*** with constant coefficients.

N.B.

For an equation of the form;

$$y'' + py' + qy = 0 \qquad (6)$$

where p and q are constant

The general solution is

$$y = e^{sx} \qquad (7)$$

From (2) in (1)

$$s^2e^{sx} + pse^{sx} + qe^{sx} = 0 \qquad (8)$$

or

$$s^2 + ps + q = 0 \qquad (9)$$

This equation is called the ***auxiliary equation*** which is a quadratic equation with two roots s_1 and s_2 that, provided $s_1 \neq s_2$, give two independent solutions. Thus the general solution of (6) is

$$y = C_1e^{s_1x} + C_2e^{s_2x}$$

Where C_1 and C_2 are constants.

The auxiliary equation gives:

$$s^2 + \frac{2mE}{\hbar^2} = 0$$

$$s^2 = -\frac{2mE}{\hbar^2}$$

$$s = \pm \frac{\sqrt{-2mE}}{\hbar}$$

$$s = \pm \frac{i\sqrt{2mE}}{\hbar} \qquad (10)$$

Since the general solution of (8) is

$$y = C_1 e^{s_1 x} + C_2 e^{s_2 x} \quad (11)$$

From (10) in (11):

$$\Psi = C_1 e^{\frac{i\sqrt{2mE}\,x}{\hbar}} + C_2 e^{-\frac{i\sqrt{2mE}\,x}{\hbar}} \quad (12)$$

Let $\frac{\sqrt{2mE}\,x}{\hbar} = \theta$ (13)

$$\Psi = C_1 e^{i\theta} + C_2 e^{-i\theta} \quad (14)$$

But from the basis of complex numbers, we have

$$e^{i\theta} = cos\ \theta + i\ sin\ \theta$$

$$e^{-i\theta} = cos\ (-\theta) + i\ sin\ (-\theta)$$

$$e^{-i\theta} = cos\ \theta - i\ sin\ \theta \quad (15)$$

From (15) in (14):

$$\Psi = C_1[cos\ \theta + i\ sin\theta] + C_2[cos\ \theta - i\ sin\theta]$$

$$\Psi = C_1 cos\,\theta + i\ C_1 sin\,\theta + C_2 cos\,\theta - i\ C_2 sin\,\theta$$

$$\Psi = (C_1 + C_2) cos\,\theta + (i\ C_1 - i\ C_2)\ sin\,\theta$$

$$\Psi = A\,cos\,\theta + B\ sin\,\theta \quad (16)$$

Where *A* and *B* are constants.

Substituting for θ from (12) in (16) we get:

$$\Psi = A\,cos\left[\hbar^{-1}\sqrt{2mE}\ x\right] + B\ sin\left[\hbar^{-1}\sqrt{2mE}\ x\right] \quad (17)$$

Where ***E*** is the total energy.

✸ **Now, we want to determine the values of A and B:**

This is done by applying the concept of ***boundary conditions*** which ***specify*** the ***value*** of the ***function***, (here ψ), or various of its ***derivatives*** at a ***point*** or ***points***.

✸**Mathematical derivative:**

Since ψ should be continuous, thus, at the *point*, *x=0*, the ψ_{I} and ψ_{II} must *approach the same value* at *x*=0. i.e.,

$$\lim_{x\to 0} \Psi_I = \lim_{x\to 0} \Psi_{II}$$

$$0 = \lim_{x\to 0} \left\{A\cos\left[\hbar^{-1}\sqrt{2mE}\ x\right] + B\ \sin\left[\hbar^{-1}\sqrt{2mE}\ x\right]\right\} \quad (18)$$

Since cos(0) = 1 , sin(0) = 0 (19)

From (18) in (19):

0 =A (20)

From (20) in (17) we get,

$$\Psi_{II} = B\ \sin\left[\hbar^{-1}\sqrt{2mE}\ x\right]$$

$$\Psi_{II} = B\ \sin\left[\frac{1}{\hbar}\sqrt{2mE}\ x\right]$$

$$\Psi_{II} = B\ \sin\left[\frac{2\pi}{h}\sqrt{2mE}\ x\right] \quad (21)$$

Similarly, if we apply the boundary conditions at x = *l*, we get,

$$\lim_{x\to l} \Psi_I = \lim_{x\to l} \Psi_{II}$$

$$0 = B\ \sin\left[\frac{2\pi}{h}\sqrt{2mE}\ l\right]$$

Since B can not be zero, because this leads to ψ is zero everywhere and thus we have an empty box. Thus;

$$0 = sin\left[\frac{2\pi}{h}\sqrt{2mE}\ l\right]$$

The zeros of sin function occur at 0, ± π, ±2 π, ± 3π, ± nπ. i.e.,

$$\left(\frac{2\pi}{h}\right)\sqrt{2mE}\ l = \pm n\pi, \qquad \text{or}$$

$$\left(\frac{2\pi}{h}\right)\sqrt{2mE} = \pm\frac{n\pi}{l} \tag{22}$$

$$\left(\frac{4\pi^2}{h^2}\right)(2mE\ )l^2 = n^2\pi^2$$

And thus

$$E = \frac{n^2\ h^2}{8\ m\ l^2}, \text{ n=1, 2, 3, …} \tag{23}$$

From (22) in (21) we get the wave function;

$$\Psi_{II} = B\ sin\ \left(\frac{n\pi\ x}{l}\right); \text{ n = 1, 2, 3, …} \tag{24}$$

✸✸ **Now, we want to determine the value of B:**

We use the normalization condition, i.e.,

$$\int_{-\infty}^{\infty} |\Psi|^2\ dx = 1$$

We will apply this condition to the three regions, I, II and III.

$$\int_{-\infty}^{0} |\Psi_I|^2\ dx + \int_{0}^{l} |\Psi_{II}|^2\ dx + \int_{l}^{\infty} |\Psi_{III}|^2\ dx = 1$$

$$|B|^2 \int_0^l sin^2\left(\frac{n\pi x}{l}\right) dx = 1 \tag{25}$$

But since, $sin^2\alpha = \frac{1}{2}\ [1 - cos\ \ 2\alpha]$ (26)

Substituting from (26) in (25) yields

$$\frac{1}{2}\ |B|^2\ \int_0^l \left(1\ -\ cos\frac{2n\pi x}{l}\right) dx\ = 1$$

$$\frac{1}{2}\ |B|^2\ \left[x\ -\ \frac{l}{2n\pi}\ sin\frac{2n\pi x}{l}\right]_0^l\ = 1$$

$$\frac{1}{2}\ |B|^2\ \left\{\left[l\ -\ \frac{l}{2n\pi}\ sin\frac{2n\pi l}{l}\right] - \left[0\ -\ \frac{l}{2n\pi}\ sin\,0\right]\right\} = 1$$

$$\frac{1}{2}\ |B|^2\ \{l\} = 1$$

$$|B|^2\ = \frac{2}{l}$$

or

$$|B| = \pm\sqrt{\frac{2}{l}} \tag{27}$$

The final solution of ψ is obtained by substitution from (27) in (24):

$$\Psi_{II} = \pm\sqrt{\frac{2}{l}}\ sin\ \left(\frac{n\pi\ x}{l}\right);\ \text{n} = 1, 2, 3, \ldots \tag{28}$$

The number *n* in the energies (23) and the wave functions (28) is called a *quantum number*. *Each different value of the quantum number n gives a different wave function and a different state*.

Analysis of the eigenvalue and eigenfunction of the problem:

1. *The energy eigenvalue* E_n: $E_n = \frac{n^2h^2}{8ml^2}$, $n = 1,2,3, \ldots$

What does this equation tell us?

1. There is an inverse proportionality between the energy and the mass of the particle as well as the length of the box. This is simply because the mass, *m*, of the particle appears in the denominator, for a given length of box, *the energy levels lie at lower values for heavy particles than for light particles*. Because the length of the box appears in the denominator (as l^2), as the walls become more confining (*l* smaller), the energy levels are squeezed upward.
2. Because *n* can take only integral values, the energy of the particle is quantized, meaning that it is restricted to a series of discrete values, called **energy levels**. According to classical mechanics, an object can have any value of the total energy.For example, a particle in a box could bounce from wall to wall with any speed and hence any kinetic energy. According to quantum mechanics, however, because only certain wavelengths fit into the box and each wavelength corresponds to a different energy, energy is quantized.
3. As we saw in the derivation of Energy equation$E = \frac{n^2h^2}{8ml^2}$, the energy quantization stems from the boundary conditions on the wavefunction, the constraints that the wavefunction must satisfy at different points of space (such as fitting into a container correctly). Because an electron in an atom has a wavefunction that must satisfy certain constraints in three dimensions, only some solutions of the Schrödinger equation and their corresponding energies are acceptable. We can begin to see the origin of the quantized energy levels of an atom.

We can use Eq. (23) to calculate the energy separation between two neighboring levels with quantum numbers *n* and *n* + 1:

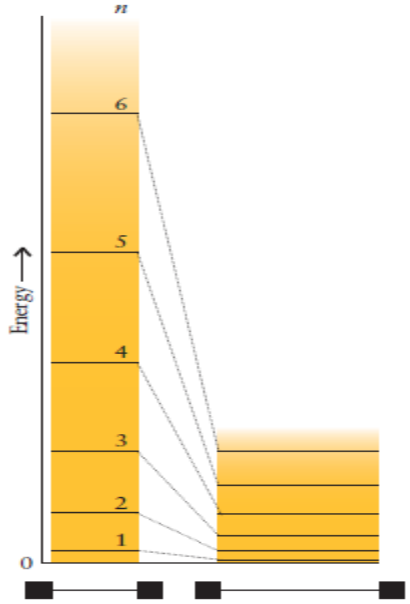
$$E_{n+1} - E_n = \frac{(n+1)^2h^2}{8ml^2} - \frac{n^2h^2}{8ml^2} = \frac{(n^2+2n+1)h^2}{8ml^2} - \frac{n^2h^2}{8ml^2}$$

$$E_{n+1} - E_n = \frac{(n^2h^2+2nh^2+h^2)}{8ml^2} - \frac{n^2h^2}{8ml^2}$$

$$E_{n+1} - E_n = \frac{(n^2h^2+2nh^2+h^2)-n^2h^2}{8ml^2} = \frac{2nh^2+h^2}{8ml^2}$$

$$E_{n+1} - E_n = (2n+1)\frac{h^2}{8ml^2}$$

We see that, as *l* (the length of the box) or *m* (the mass of the particle) increases, the separation between neighboring energy levels decreases (Fig. 3.1). That is why no one noticed that energy is quantized until they investigated very small systems such as an electron in a hydrogen atom: the separation between levels is so small for ordinary particles in ordinary- sized vessels that it is completely undetectable. We can, in fact, ignore the quantization of the motion of the atoms of a gas in a typical flask.



EXAMPLE

Suppose that the hydrogen atom is treated as a one-dimensional box of length 150 pm (the approximate diameter of the atom) containing an electron. Predict the wavelength of the radiation emitted when the electron falls to the lowest energy level from the next higher energy level. The mass of electron is 9.10939×10^{-31} kg.

Solution

The lowest energy level has *n* = 1, and so we can use Eq. 12 with *n* = 1. The energy difference is carried away as a photon of radiation; so we set the energy difference equal to $h\nu$ and express ν in terms of the corresponding wavelength by using $\lambda = \frac{c}{\nu}$.

Step 1: *n*=1, so 2*n*+1=3

$$E_2 - E_1 = (2n+1)\frac{h^2}{8ml^2} = \frac{3h^2}{8ml^2} \quad (1)$$

Step 2: the energy difference is evaluated from Planck's equation

$$\Delta E = E_2 - E_1 = h\nu \quad (2)$$

Equating eqs. (1) and (2):

$$\frac{3h^2}{8ml^2} = h\nu$$

or

$$\frac{3h}{8ml^2} = \nu = \frac{c}{\lambda} \quad (3)$$

$$\lambda = \frac{8mcl^2}{3h} \quad (4)$$

$$\lambda = \frac{8\times(9.10939\times10^{-31}\text{kg})\times(2.998\times10^{8}\text{m.s}^{-1})\times(1.50\times10^{-10}\text{m})^2}{3\times(6.626\times10^{-34}\text{J.s})}$$

$$\lambda = \frac{8\times9.10939\times10^{-31}\times2.998\times10^{8}\times(1.50\times10^{-10})^2\text{kg.m.s}^{-1}.\text{m}^2}{3\times6.626\times10^{-34}\text{kg.m}^2.\text{s}^{-2}.\text{s}}$$

$$\lambda = \frac{8\times9.10939\times2.998\times1.50\times1.5\times10^{-9}\text{ m}}{3\times6.626} = 2.47\times10^{-8}\text{m}$$

This wavelength corresponds to 24.7 nm. The experimental value for the actual transition in a hydrogen atom is 122 nm. Although there is a big discrepancy, an atom does not have the hard boundaries that confine a particle in a box, and is threedimensional. The fact that the predicted wavelength has nearly the same order of magnitude as the actual value suggests that a quantum theory of the atom, based on a more realistic three- dimensional model, should give good agreement.

4. Another surprising implication of Eq. (23) is that a particle in a container cannot have zero energy. Because the lowest value of *n* is 1 (corresponding to a wave of one-half wavelength fitting into the box), the lowest energy is $E_1 = \frac{h^2}{8ml^2}$. This lowest possible energy is called the **zero-point energy**. The existence of a zero-point energy means that, *according to quantum mechanics, a particle can never be perfectly still when it is confined between two walls*: *it must always possess an energy*—in this case, a kinetic

energy—of at least $\frac{h^2}{8ml^2}$. This result is consistent with the uncertainty principle. When a particle is confined between two walls, the uncertainty in its position cannot be larger than the distance between the two walls. Because the position is not completely uncertain, the linear momentum must be uncertain, too, and so we cannot say that the particle is completely still. The particle must therefore have some kinetic energy. The zero-point energy is a purely quantum mechanical phenomenon and is very small for macroscopic systems.

2. *The eigenfunction* ψ_n:

$$\psi = \pm\sqrt{\frac{2}{l}}sin\left(\frac{n\pi x}{l}\right) \ , n = 1,2,3, \ldots$$

The shapes of the wavefunctions of a particle in a box also reveal some interesting information. Let's look at the two lowest energy wavefunctions, corresponding to n = 1 and n = 2.

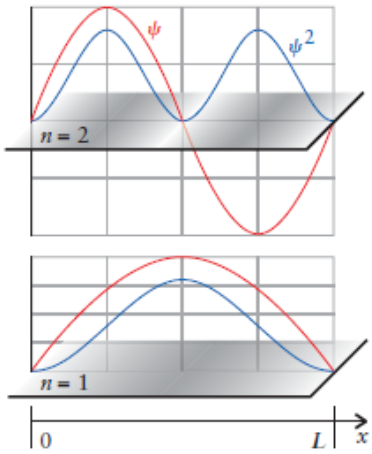


Fig. 3.2

Figure 3.2 shows by the density of shading, the likelihood of finding a particle: we see that when a particle is described by the wavefunction ψ_1 (and has energy $\frac{h^2}{8ml^2}$), then it is most likely to be found in the center of the box. Conversely, if the particle is described by the wavefunction ψ_2 (and has energy $\frac{h^2}{2ml^2}$), then it is most likely to be found in regions between the center and the walls and is unlikely to be found in the middle of the box. Remember that the wavefunction itself does not have any direct physical significance: we have to take the square of ψ before we can interpret it in terms of the probability of finding a particle somewhere.

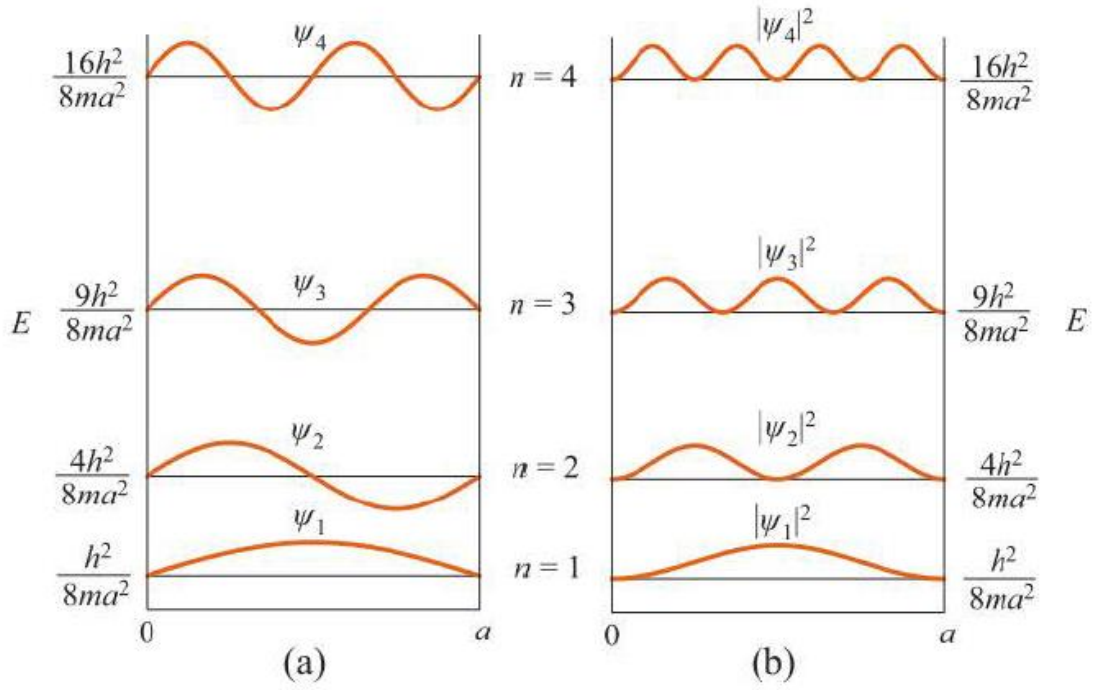


Fig3.3.: The energy levels, wave functions (a), and probability densities (b) for the particle in a box.

Discussion the results of the 1D box problem:

Since the wave function "knows" everything that can be known about the system, let's ask it some questions:

Question 1: Where is the particle?

In order to solve this question, the state function will make a comparison between the Classical and Quantum Mechanics

In Classical Mechanics:

We would expect from our experience with macroscopic objects that it could be anywhere in the box with *equal probability*.

In Quantum Mechanics:

But quantum mechanics says that the probability is equal to ψ^2 and, as can be seen on Figures 3.4 and 3.4, this probability is by no means uniform.

For the *n*= 1 state the probability is greatest in the center at$x = \frac{l}{2}$.

For *n*= 2 the probability is greatest for $x = \frac{l}{4}$ and$x = \frac{3l}{4}$: the probability of being at $x = \frac{l}{2}$ is zero – there is a ***node*** in the center of the box.

The ***node*** is that position at which the probability of finding the particle is zero.

For larger quantum numbers, the probability becomes more uniform and closer to our expectations. This is an example of the **Bohr correspondence principle:**

Quantum mechanics approaches classical mechanics in the limit of large quantum numbers.

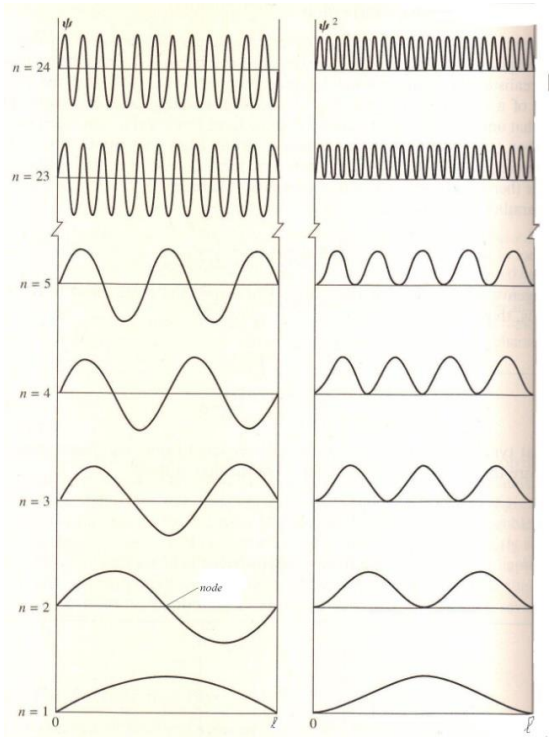


Fig. 3.4

Question 2: is the Bohr correspondence principle is applied for calculating the energy?

Another classical expectation is that the energy is not quantized, the energy levels are too close to being observed separately. For macroscopic-size boxes or objects the *box constant*, $\frac{h^2}{8\mathrm{m}a^2}$, is very small and gigantic quantum numbers are required to obtain any significant amount of energy. However, the 1-dimensional particle in a box fails this test because the energy-level separation increases (as n^2) with large quantum numbers and the Bohr

correspondence principle is not obeyed. This problem is an artifact of our artificially limiting the particle to one dimension, and goes away when the more realistic 3-dimensional box is considered.

Question 3: How fast is the particle moving?

If we calculate the expectation value of the momentum, the result is zero. From the average-value theorem, we have

$$\langle \hat{p}_x \rangle = \int_0^l \psi_n^* (\hat{p}_x \psi_n) dx = \int_0^l \sqrt{\frac{2}{l}} \, sin\left(\frac{n\pi x}{l}\right) . \left[\frac{\hbar}{i}\frac{\partial}{\partial x}\left(\sqrt{\frac{2}{l}} \, sin\left(\frac{n\pi x}{l}\right)\right)\right] dx$$

$$\langle \hat{p}_x \rangle = \frac{2}{l}\frac{\hbar}{i}\int_0^l sin\left(\frac{n\pi x}{l}\right) . \frac{d}{dx}\left(sin\left(\frac{n\pi x}{l}\right)\right) dx$$

$$\langle \hat{p}_x \rangle = \frac{2}{l}\frac{\hbar}{i}\frac{n\pi}{l}\int_0^l sin\left(\frac{n\pi x}{l}\right) \, cos\left(\frac{n\pi x}{l}\right) dx = 0$$

This does not mean that the particle is standing still, but only that it is equally likely to be moving in either direction, positive or negative. The speed can be estimated either, directly from the total energy equation or from the average squared momentum, $\langle \hat{p}_x^2 \rangle$ as follows:

(1) From the energy equation:

Total energy = Kinetic energy + potential energy

$E = K + V(x)$; $V(x)=0$

$$\frac{n^2h^2}{8ml^2} = \frac{1}{2}mv^2$$

$$\frac{n^2h^2}{4ml^2} = mv^2$$

$$v^2 = \frac{n^2h^2}{4m^2l^2}$$

$$v = \pm\sqrt{\frac{n^2h^2}{4m^2l^2}} = \pm\frac{nh}{2ml}$$

(2) From the average squared momentum, $\langle \hat{p}_x^2 \rangle$:

$\langle \hat{p}_x^2 \rangle = 2mE = \frac{n^2h^2}{4l^2}$; $|\hat{p}_x| = \frac{nh}{2l}$

This result suggests that the speed is

$$v = \frac{nh}{2ml}$$

Since the *minimum value* of the quantum number *n* is 1, the preceding result suggests that a confined object cannot sit still: there is a minimum velocity. The smallness of Planck's constant guarantees that this minimum velocity is negligible for macroscopic-sized objects (where it has never been observed).

Example: Calculate the minimum velocity for a 1g mass in a 1cm box.

The minimum velocity is:

$$v_{min} = \pm\frac{nh}{2ml}\,; n = 1$$

$$v_{min} = \pm\frac{(1)(6.626 \times 10^{-34}\text{kg.m}^2.\text{s}^{-1})}{(2)(1 \times 10^{-3}\text{kg})(1 \times 10^{-2}\text{m})} = 3.313 \times 10^{-29}\text{m.s}^{-1}$$

This is about 10^{-19}m, less than the width of an atomic nucleus, *per century*!

For an electron in a 1-bohr box, the above example, the minimum velocity is 6.87×10^6 m/s. For a proton in a box of that size, it is 3743m/s.

That there is a minimum velocity/momentum is in accordance with the Heisenberg uncertainty principle. Since the momentum could be either positive or negative, there is an uncertainty in its value:

$p_x = \pm\frac{nh}{2l}$ and $\Delta p_x = \frac{nh}{l}$

The uncertainty in the position is the length of the box at most; therefore with $\Delta x = l$;

$\Delta p_x \Delta x = nh$

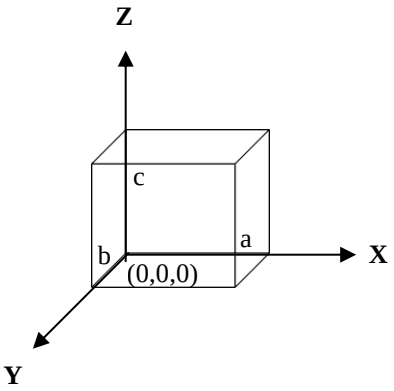
The minimum value is for *n*=1, so Heisenberg's uncertainty principle is obeyed. i.e., $\Delta p_x \Delta x = h$.

2. The particle in a three-dimensional box

For simply, we will consider only the case of one-particle system.

✸***Coordinate system:***

The origin being at one corner.



✸***Potential energy:***

(a) outside the box: $V_{xyz} = \infty$

(b) inside the box: $V_{xyz} = 0$

$V(x,y,z)=0$ in the region $\begin{cases} 0 < x < a \\ 0 < y < b \\ 0 < z < c \end{cases}$

We have to calculate ψ and E in – and out-side the box:

1. outside the box:

$V(x,y,z) = \infty$ and since a particle can not have infinite energy; thus, the probability of finding the particle outside the box is zero. i.e.,

$|\Psi|^2 = 0$ and $\psi = 0$.

2. Inside the box:

We begin the solution with writing the Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z) \quad (1)$$

Inside the box regions; $V(x,y,z) = 0$ (2)

From (2) in (1)

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + 0 \quad (3)$$

Or

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + 0$$

The simplest form of the time-independent Schrödinger equation is

$$\hat{H}\psi = E\psi \qquad (4)$$

Substituting from (3) in (4):

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = E\psi \qquad (5)$$

The operator ∇^2 is a sum of three independent terms, each containing derivatives with respect to only one of the Cartesian coordinates. In this case, it is a general rule that, the state function can be written as a product, i.e.,

$$\psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z) \quad \text{"Separation of variable"} \qquad (6)$$

General rule:

Whenever, the operator is a sum of independent terms, the eigenfunctions can be written as a product.

Moreover, the operator $\frac{\partial}{\partial x}$ is a derivative holding *y* and *z* constant. Therefore, partial derivatives of (6) yields:

$$\frac{\partial^2}{\partial x^2}(\psi_x\psi_y\psi_z) = \psi_y\psi_z\frac{\partial^2\psi}{\partial x^2} = \psi_y\psi_z\psi_x^{``}$$

$$\frac{\partial^2}{\partial y^2}(\psi_x\psi_y\psi_z) = \psi_x\psi_z\frac{\partial^2\psi}{\partial y^2} = \psi_x\psi_z\psi_y^{``}$$

$$\frac{\partial^2}{\partial z^2}(\psi_x\psi_y\psi_z) = \psi_x\psi_y\frac{\partial^2\psi}{\partial z^2} = \psi_x\psi_y\psi_z^{``} \qquad (7)$$

Substitution of (6) and (7) into (5) gives:

$$-\frac{\hbar^2}{2m}\left[\psi_y\psi_z\psi_x^{``} + \psi_x\psi_z\psi_y^{``} + \psi_x\psi_y\psi_z^{``}\right] = E\psi_x\psi_y\psi_z \qquad (8)$$

Dividing by $\psi(x,y,z) = \psi_x\psi_y\psi_z$ gives:

$$-\frac{\hbar^2}{2m}\left[\frac{\ddot{\psi_x}}{\psi_x}+\frac{\ddot{\psi_y}}{\psi_y}+\frac{\ddot{\psi_z}}{\psi_z}\right]=E \qquad (9)$$

This equation is of the form:

$f(x) + g(y) + h(z) = \text{constant}$ (10)

Because *x*, *y*, and *z* are independent variable, we shall see that each term of this equation must be constant.

Suppose we vary *x* to *x*+d*x*, holding *y* and *z* constant, eq. (10) becomes:

$f(x + dx) + g(y) + h(z) = \text{constant}$ (11)

Subtracting (10) from (11)

$f(x + dx) - f(x) = 0$

or $\frac{df}{dx} = cons\,tan\,t$ (12)

The solution of Eq. (12) is $f(x)$ = constant. Therefore, the ***R.H.S.*** of Eq. (9) can be written as a ***sum*** of ***three*** constants, i.e.,

$E = E_x + E_y + E_z$ (13)

Since ***each term*** on the ***L.H.S.*** must be ***constant***, Eq. (9) becomes three separate equations as follows:

$-\frac{\hbar^2}{2m}\frac{\ddot{\psi_x}}{\psi_x} = E_x$ or $\frac{d^2\psi_x}{dx^2} = -\frac{2mE_x}{\hbar^2}\psi_x$ or

$\frac{d^2\psi_x}{dx^2}+\frac{2mE_x}{\hbar^2}\psi_x = 0$ (14)

Similarly;

$\frac{d^2\psi_y}{dy^2}+\frac{2mE_y}{\hbar^2}\psi_y = 0$ (15)

$\frac{d^2\psi_z}{dz^2}+\frac{2mE_z}{\hbar^2}\psi_z = 0$ (16)

Since Eqs. (14, 15 and 16) are the Schrödinger equation for a particle in a one-dimensional box, thus, the solution of these equations are:

$$\psi_x = \sqrt{\frac{2}{a}}\, sin\left(\frac{n_x \pi x}{a}\right) \tag{17}$$

$$E_x = \frac{n_x^2 h^2}{8ma^2} \tag{18}$$

$$\psi_y = \sqrt{\frac{2}{b}}\, sin\left(\frac{n_y \pi y}{b}\right) \tag{19}$$

$$E_y = \frac{n_y^2 h^2}{8mb^2} \tag{20}$$

$$\psi_z = \sqrt{\frac{2}{c}}\, sin\left(\frac{n_z \pi z}{c}\right) \tag{21}$$

$$E_z = \frac{n_z^2 h^2}{8mc^2} \tag{22}$$

where n_x, n_y, n_z = 1, 2, 3, …

Therefore, the total energy, E, can be found by substituting for E_x, E_y, E_z from Eqs. (18, 20 and 22) in Eq. (13):

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

If $a = b = c$ "i.e., the box is a cube"

$$E = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{23}$$

The presence of three quantum numbers n_x, n_y, n_z is attributed to the three-dimensional nature of the problem. The three quantum numbers vary independently of one another.

Since the state function is a product, from Eq. (6), thus, substituting for ψ_x, ψ_y, and ψ_z in Eq. (6) from Eqs. (17,19, and 21), we get,

$$\psi(x,y,z) = \sqrt{\frac{2}{a}} sin\left(\frac{n_x \pi x}{a}\right) \sqrt{\frac{2}{b}} sin\left(\frac{n_y \pi y}{b}\right) \sqrt{\frac{2}{c}} sin\left(\frac{n_z \pi z}{c}\right)$$

$$\psi(x,y,z) = \sqrt{\frac{8}{abc}} sin\left(\frac{n_x \pi x}{a}\right) sin\left(\frac{n_y \pi y}{b}\right) sin\left(\frac{n_z \pi z}{c}\right) \quad (24)$$

✹Special case; if *a*=*b*=*c* "i.e., a cube" Eq. (13) becomes;

$$\psi(x,y,z) = \sqrt{\frac{8}{a^3}} sin\left(\frac{n_x \pi x}{a}\right) sin\left(\frac{n_y \pi y}{a}\right) sin\left(\frac{n_z \pi z}{a}\right) \quad (25)$$

N.B.

Since the factors of *x*, *y* and *z* in the wave function are each independently normalized, the wave function is normalized, i.e,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi|^2 dxdydz = \int_0^a |\psi_x(x)|^2 dx \int_0^a \left|\psi_y(y)\right|^2 dy \int_0^a |\psi_z(z)|^2 dz = 1$$

Where we used;

$$\iiint \psi_x(x)\psi_y(y)\psi_z(z)dxdydz = \int \psi_x(x)\,dx \int \psi_y(y)\,dy \int \psi_z(z)\,dz$$

What are the lessons we can learn from the energy and wavefunction equations?

The energy equations (22 and 23) and the wavefunction equations (24 and 25) tell us the following important lessons:

1. If a Hamiltonian of several coordinates is separable into a sum of one-coordinate terms, the total wavefunction is a product of the individual wavefunctions for each coordinate, and the total energy is the sum of the independent coordinate energies.
2. There is a zero-point energy for each coordinate. As long as the box is bound by walls along x, the lowest energy state has some non-zero value of E_x. The same holds for the *y* and *z* axes.
3. It is possible to have several states with different quantum numbers, and therefore different wavefunctions, but with the same energy.

Degeneracy:

Each quantum number may take a value of 1,2,3, …, ∞.

Each set of quantum numbers defines an independent state which will be denoted as (n_x,n_y,n_z).

The following table presents some of the allowed energies of a particle confined to a cube with infinitely strong walls:

Table (1.2): *Energy levels and degeneracies for the particle in a box:*

States (n_x,n_y,n_z)	Energy $\frac{8m^2a^2}{h^2}$	Degeneracy (d)	States (n_x,n_y,n_z)	Energy $\frac{8m^2a^2}{h^2}$	Degeneracy (d)
(1,1,1)	3	1	(1,1,3)	11	3
			(1,3,1)	11	
			(3,1,1)	11	
(2,1,1)	6		(2,2,2)	12	1
(1,2,1)	6	3			
(1,1,2)	6				
(1,2,2)	9		(3,2,1)	14	
(2,1,2)	9	3	(3,1,2)	14	
(2,2,1)	9		(1,2,3)	14	6
			(1,3,2)	14	
			(2,1,3)	14	
			(2,3,1)	14	

It is clear that, there are *states* with *different quantum numbers* but have the same energy, e.g., ψ_{211}, ψ_{121}, ψ_{112}. Since equation (13) implies that these three sets of quantum numbers give three *different independent* wave *functions* and therefore, represents different states of the system.

Definition:

When two or more independent wave functions correspond to states with the same energy eigenvalue, the *eigenvalue* is said to be *degenerate* or *isoenergetic*.

Degree of degeneracy (g) or "degeneracy":

The degeneracy of an energy level is the number of states that have the same energy.

Therefore, the energy level, $E = 6\left(\frac{h^2}{8ma^2}\right)$ is said to be 3-fold degenerate, i.e., g=3.

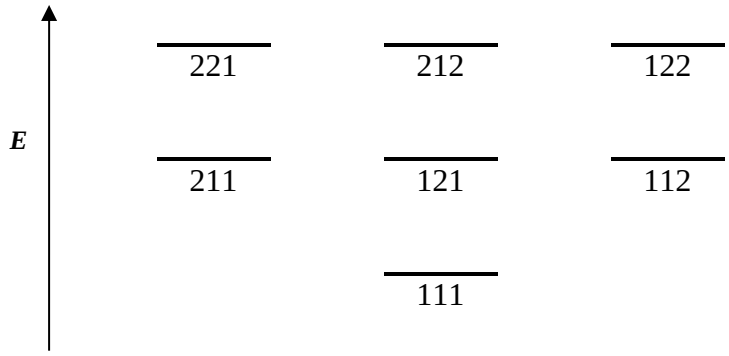


Fig. (2.1): *Lowest few stationary states for a particle in a cubic box.*

Some important observations:

1. Since the degeneracy is occurred when we made the edges of the box equal, thus, *degeneracy is usually related to the symmetry of the system.*
2. The functions ψ_{211}, ψ_{121}, ψ_{112} can be transformed into one another by rotating the cubic box.
3. Usually, degerneracy does not occur in one-dimensional sysytem.
4. In quantum mechanics, the terms "state" and "energy level" have different meaning as follows:

A stationary state:

✸Is *specified* by giving the *wave function* ψ.

✸Each *different* ψ is a *different state*.

An energy level:

✸Is *specified* by giving the *value of the energy*.

✸Each *different value* of E is a *different energy level*.

Example:

The ψ_{211} state has zero probability density of finding the particle at $x = \frac{a}{2}$.

The ψ_{121} state has a maximum probability density at $x = \frac{a}{2}$.

Physical meaning of degeneracy:

From table (1.2), it is clear that, the density of energy levels "the number of states in a fixed interval ΔE" is increasing.

The importance of this fact is that; since macroscopic objects are not observed to have quantized energies – all velocities seem to be possible. In accordance with Bohr correspondence principle, the state density for large quantum numbers is so large that, effectively, any velocity is possible.

3. The solution of Schrödinger equation for the one-electron Atoms

The aim of this lecture is to explain how the modern chemists used the mathematical model just we learned (postulates of quantum mechanics) to describe one-electron atoms. Since atoms are the building blocks to construct molecules, we need to build up a reliable description of atoms.

Atoms and the chemical bonds that they form are three- dimensional. Now, with the tools of quantum mechanics at our hands, we return to the structure of atoms and are able to describe them more accurately. To do this, our task is to find the energies (eigenvalues) and wavefunctions (eigenstates).

To describe the three-dimensional nature of the electron's wavelike properties, we now liberate the electron from a circular orbit and allow it to have density anywhere: along a circular path, out of the plane of that circle, and even at different distances from the nucleus — all while it's in a single quantum state. Let the circular orbit in the Bohr model correspond to motion along an angle ϕ, measured from the x axis in the xy plane. Now we need to introduce two new coordinates to accommodate the new motions permitted to the electron. We will call the new coordinates θ (the angle measured in any direction from the z axis) and r (the distance from the center of mass, which is roughly at the nucleus). Fig. 3.1 provides definitions for these spherical coordinates.

The relation between cartesian and spherical coordinates is:

$x = r\sin\theta\cos\phi\,, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta$

$r^2 = x^2 + y^2 + z^2$

The ranges of the coordinates are

$0 \le r \le \infty, \;\; 0 \le \theta \le \pi, \;\; 0 \le \phi \le 2\pi$

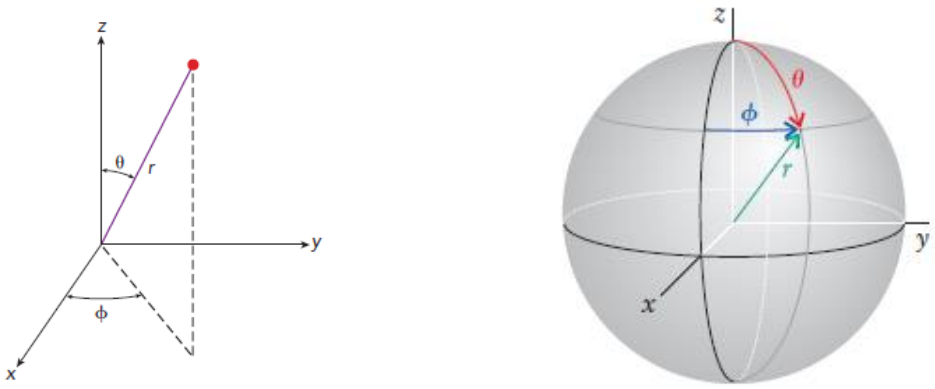


Figure 1: Relation between spherical and Cartesian coordinates

We need a way to identify the location of each point around a nucleus. It is most convenient to describe these locations in terms of spherical polar coordinates, in which each point is labeled with three coordinates:

1. *r*, the distance from the center of the atom;
2. θ (theta), the angle from the positive z-axis (the "north pole"), which can be thought of as playing the role of the geographical "latitude"; and
3. ϕ (phi), the angle about the z-axis, the geographical "longitude."

Each independent coordinate along which the electron can move is an electronic degree of freedom, a different way that the electron can store its energy. In the semiclassical Bohr model, the electron could travel only along the coordinate ϕ, tracing out a circular path. Now, with motion allowed in all three directions, the energy may be divided among the different degrees of freedom: r, θ, and ϕ (Fig. 3.2).

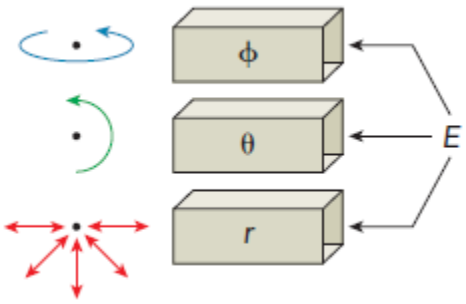


Figure 2 Energy is expressed as motion along different coordinates. Real electrons exist in three dimensions and can move along ϕ, θ, or r. Each coordinate provides a different degree of freedom for the electron, like a set of different boxes in which the energy can be stored. In general, some of the energy may go into each of the three degrees of freedom.

When we apply the de Broglie electron/wave to Bohr's circular orbit, we find some similarities to the particle-in-a-box wavefunction. Those similarities remain, now that we extend the electron's motion to r and θ. For example,

• The electron is not a point particle in this system. It behaves instead like a cloud of mass and charge, with its density diminishing as the potential energy climbs at distances far from the nucleus.

• As we put more energy into one degree of freedom, the number of nodes along that coordinate increases. There may be nodes at particular distances r from the nucleus, as well as at certain angles ϕ or θ. As we saw for the particle in a three-dimensional box, some wavefunctions will have nodes along all three coordinates.

• Also as with the three-dimensional box, we expect that as we increase the energy in the system, there will be ever more states to choose from, leading to a greater degeneracy g.

The system will have some new features as well. For example—here's a surprise— the electron doesn't need to orbit the nucleus at all, meaning that the angular momentum can be zero. That is because we now have radial kinetic energy for motion along r, and that motion alone is sufficient to keep the electron in a stable distribution about the nucleus. If we imagine the Coulomb potential as a bowl with the nucleus at the bottom, Bohr's orbits correspond to rolling the electron like a marble along the lip of the bowl at some fixed speed and always the same distance from the nucleus, so that only the angle ϕ changes. But we can also allow the marble to roll from one end of the bowl to the other, across the middle; there is no angular motion in this case, only radial motion (Fig. 3.3).

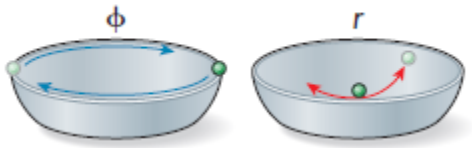


Figure 3.3: Angular and radial motion. For a marble rolling around the rim of a bowl along angleϕ, we can measure the values of the kinetic energy and the angular momentum. If we instead roll the marble from one side of the bowl through the middle and to the other side, then the motion is along the distance r from the center of the bowl. Both motions may have the same kinetic energy, but the radial motion has no angular momentum.

We can put the same kinetic energy into the radial motion, but the angular momentum is now zero. In the same way, the electron can oscillate along r without motion along the angular coordinates θ or ϕ, although most of the quantum states we find will involve some combination of radial and angular motion.

The One-Electron Atom Schrödinger Equation

Our system is an electron and an atomic nucleus interacting through the Coulomb potential. Our task is to solve the Schrödinger equation (eigenvalue equation) for this system. The First step in the solution is writing the Hamiltonian operatorfor this system. As we know, this operator is a compound one, i.e., consisting of the kinetic and potential energy operators.

1. ***The kinetic energy operator*** for motion in three dimensions can be applied to both the nucleus and electron. Then we can obtain a total kinetic energy operator

$$\hat{K} = \hat{K}_{\text{nuc}} + \hat{K}_{\text{elec}}$$

$$\hat{K} = -\frac{\hbar^2}{2m_{\text{nuc}}}\nabla^2_{\text{nuc}} - \frac{\hbar^2}{2m_{\text{e}}}\nabla^2_{\text{elec}} \qquad (1)$$

Where m_{nuc} and ∇^2_{nuc} stand for the mass and Laplacian of the nucleus, and m_{e} and Laplacian ∇^2_{elec} for the electron.

This form of kinetic energy operator deals with all the motions of the two particles constituting the system. However, we don't care with the overall motion of the whole atom; rather we are interested in the motion of the electron relative to the nucleus. A common transformation in physics allows us to rearrange the kinetic energy terms for the nucleus and the electron into a reduced mass term for the relative motions, with the reduced mass $\mu = \frac{m_{\text{nuc}}m_e}{m_{\text{nuc}}+m_e}$, and a center of mass term for the overall motion, with mass $m_{\text{nuc}} + m_{\text{e}}$:

$$\hat{K} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{\hbar^2}{2(m_{\text{nuc}}+m_{\text{e}})}\nabla^2_{\text{COM}} \qquad (2)$$

We will ignore the center of mass term for now to focus on the relative motions of the particles. Furthermore, the nucleus is always at least 1800 times more massive than the electron. So the center of mass — to a good approximation — is at the nucleus. That means that the motions relative to the center of mass are the motions of the electron, and the reduced mass can be approximated by the mass of the electron:

$$\mu = \frac{m_{\text{nuc}}m_e}{m_{\text{nuc}}+m_e} \approx \frac{m_{\text{nuc}}m_e}{m_{\text{nuc}}} = m_e \qquad (3)$$

Therefore, our kinetic energy operator starts off in this form:

$$\hat{K} = -\frac{\hbar^2}{2m_{\text{e}}}\nabla^2 \qquad (4)$$

We have to make one major adjustment before proceeding: we have to figure out the best way to write the Laplacian, ∇^2. For atomic systems, spherical coordinates are much more convenient to use than Cartesian coordinates.

The kinetic energy operator is most easily written in terms of *x*, *y*, and *z* because motion is linear when no forces are at work. But in this chapter, we do have a force at work: the Coulomb attraction of the electron for the nucleus — a force that depends only on the distance *r*, a spherical coordinate. So we have a choice: the kinetic energy operator is expressed most simply in Cartesian coordinates, and the potential energy in spherical coordinates. The coordinates convenient for the potential function win out. *The motions of the electron, and therefore the shapes of its wavefunctions, are determined by the Coulomb force, and by using the coordinates convenient for U we will obtain wavefunctions in the most convenient coordinates as well.*

With a lot of trigonometry, you could show that the Laplacian in spherical coordinates is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2} \qquad (5)$$

The Laplacian finds the curvature of the wavefunction by taking the second derivative. The greater the curvature, the faster the wavefunction oscillates and the shorter the de Broglie wavelength $\lambda = \frac{h}{mv} = \frac{h}{p}$. The de Broglie wavelength, in turn, relates the wavefunction to the momentum *p*. In this way, the Laplacian effectively extracts the kinetic energy, $K = \frac{p^2}{2m}$, from the wavefunction.

The coordinate conversion doesn't affect the physics that ∇^2 represents. We can see in Eq. (5) that the Laplacian is still a sum over three second derivatives, and each term still has units of (distance)$^{-2}$. Combining Eqs. (4) and (5), we obtain the kinetic energy operator in spherical coordinates:

$$\hat{K} = -\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right]$$

$$\hat{K} = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{2m_e r^2}\hat{L}^2(\theta,\phi) \qquad (6)$$

where

$$\hat{L}^2(\theta,\phi) = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad (7)$$

The $\hat{L}^2$ term contains all the dependence on the angular motion of the electron.

N.B.

In CM, we express the kinetic energy of a particle as $\frac{1}{2}mv^2$, and we can break the contributions to the velocity up into a radial speed v_r and an angular speed $v_{\theta,\phi}$, which allows us to obtain the kinetic energy in a form similar to the quantum kinetic energy operator in Eq. (7):

$$K = \frac{mv^2}{2} = \frac{mv_r^2}{2} + \frac{mv_{\theta,\phi}^2}{2} = \frac{mv_r^2}{2} + \frac{(mrv_{\theta,\phi})^2}{2mr^2} = \frac{mv_r^2}{2} + \frac{L^2}{2mr^2} \quad (8)$$

$$L = mrv_{\theta,\phi}$$

where L is the angular momentum. By analogy between Eqs. (6) and (8), let us claim that the eigenvalue of the operator $\hat{L}^2(\theta,\phi)$ is indeed L^2, the square of the angular momentum.

2. ***The potential energy*** is the Coulomb energy for the interaction between two point charges where we set the charges equal to *Ze* for the nucleus and - *e* for the electron:

$$V = \frac{(Ze)(-e)}{4\pi\varepsilon_0 r_{12}} = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad (8)$$

Combining the kinetic (Eq. 7) and potential (Eq. 8) energy operators, the Hamiltonian for the one-electron atom becomes:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{2m_e r^2}\hat{L}^2(\theta,\phi) - \frac{Ze^2}{4\pi\varepsilon_0 r} \quad (9)$$

Solving the Schrödinger equation:

The Hamiltonian here does not have so straightforward a separation of variables as we have in the three-dimensional box problem, because the three variables (r, θ, and ϕ) do not each appear alone in separate terms of the Hamiltonian. Instead, the derivative with respect to ϕ is multiplied by a function of θ, and the θ- and ϕ-dependent parts of the Hamiltonian are then together multiplied by a function of r. The problem is still separable, but to a lesser degree. Rather than solving the three parts independently, the way we did with the three-dimensional box, we solve this Schrödinger equation by a specific sequence of steps. At each step, we

replace an operator that depends on a specific coordinate (like θ or ϕ) with the operator's eigenvalue, which has a numerical value for a particular quantum state. We say that we replace the explicit dependence of the Hamiltonian on θ and ϕ by an implicit dependence, where θ and ϕ have determined certain numerical values in the Hamiltonian but no longer appear directly in the expression themselves. Here are the steps:

• Start with ϕ by finding the eigenvalues and eigenstates of $\frac{\partial^2}{\partial\phi^2}$, and then replace that operator with its eigenvalues so that $\hat{L}^2$ now depends only on θ.

• Next solve the θ-part by finding the eigenvalues and eigenstates of $\hat{L}^2$, and replace that operator with its eigenvalues so that $\hat{H}$ now depends only on *r*.

• Finally, solve the differential equation in *r* to get the radial wavefunctions and energies of the electron.

Only the last step actually solves the Schrödinger equation, with the final eigenvalues being the energies, but the eigenstates we find along the way will each contribute to the final wavefunctions.

We will focus on this Schrödinger equation more closely than on any other, *because these energies and wavefunctions are the fundamental results from quantum mechanics that we use in chemistry*. **The angular part** of the atomic wavefunction is predominantly **responsible for the geometries of covalently bonded molecules**. **The radial part** of the wavefunction effectively **sets the size of the atom, and consequently controls the onset of steric interactions**, among many other properties of molecules.

However, for simplicity, we will omit the mathematical derivations, and will get the final solutions and then discuss it.

The solution of the angular wavefunction:

Combining the two angular parts, $\Theta(\theta)$ and $\Phi(\phi)$, we obtain the eigenfunctions of $\hat{L}^2(\theta,\phi)$, which are a class of functions called the **spherical harmonics,**

$$Y_l^{m_l}(\theta,\phi) = \Theta(\theta)\Phi(\phi) = A_{l,m_l}P_l^{m_l}(\theta)e^{im_l\phi}$$

The solution of the radial wavefunction:

The general radial wavefunction may be written

$$R_{n,l}(r) = A_{n,l}e^{-Zr/(na_0)}\left(\frac{Zr}{a_0}\right)^l \mathcal{L}_{n-l-1}(r)$$

The quantity a_0 is called the Bohr radius; when the values of the fundamental constants are inserted, we find a_0 = 52.9 pm.

The one-electron atom orbital wavefunctions:

The combined ***wavefunction***, is

$$\psi_{n,l,m_l} = R_{n,l}(r)Y_l^{m_l}(\theta,\phi) = A_{n,l,m_l}e^{-Zr/(na_0)}\left(\frac{Zr}{a_0}\right)^l \mathcal{L}_{n-l-1}(r)\mathcal{P}_l^{m_l}(\theta)e^{im_l\phi}$$

With ***energies***:

$$E_n = -\frac{Z^2}{2n^2}E_h = -\frac{\hbar^2}{2m_e}\left(\frac{Z}{na_0}\right)^2 = -\frac{h^2}{8\pi^2 m_e}\left(\frac{Z}{na_0}\right)^2$$

Given values of l and m_l, we can find $P_l^{m_l}(\theta)$, which presented in Table (1) for some values of l and m_l. Polar plots of these functions in the xz plane are given in Fig. 3.6. We have shown that the eigenvalue for the operator $\hat{L}^2(\theta,\phi)$ is $\hbar^2 l(l+1)$, the square of the orbital angular momentum. Hence, the angular momentum L has a magnitude equal to $\hbar\sqrt{l(l+1)}$.

Table 1: Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions

n	***l***	$R_{nl}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3-\frac{2Zr}{a_0}+\frac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$
	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$
4	0	$\frac{1}{4}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{3Zr}{4a_0}+\frac{Z^2r^2}{8a_0^2}-\frac{Z^3r^3}{192a_0^3}\right)e^{-Zr/4a_0}$
4	1	$\frac{\sqrt{5}}{16\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Z}{a_0}\right)\left(1-\frac{Zr}{4a_0}+\frac{Z^2r^2}{8a_0^2}\right)e^{-Zr/4a_0}$

4	2	$\frac{1}{64\sqrt{5}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Z}{a_0}\right)^{2}\left(1-\frac{Zr}{12a_0}\right)e^{-Zr/4a_0}$
4	3	$\frac{1}{768\sqrt{35}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^{3}e^{-Zr/4a_0}$

*Note: In each case, $a_0 = \frac{4\pi\varepsilon_0^2}{m_e e^2}$, or close to 52.9 pm; for hydrogen itself, Z=1.

(b) The angular wavefunctions $Y_l^{m_l}(\theta,\phi)$of the one-electron atom:

l	**(m_l)***		$\boldsymbol{Y_l^{m_l}(\theta,\phi)}$
0	0		$\sqrt{\frac{1}{4\pi}}$
1	0	z	$\sqrt{\frac{3}{4\pi}}cos\,\theta$
1	±1		$\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	z^2	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
2	±1		$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2		$\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0		$\sqrt{\frac{7}{16\pi}}\cos\theta\,(5\cos^2\theta-3)$
3	±1		$\sqrt{\frac{21}{64\pi}}\sin\theta\,(5\cos^2\theta-1)e^{\pm i\phi}$
3	±2		$\sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3		$\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

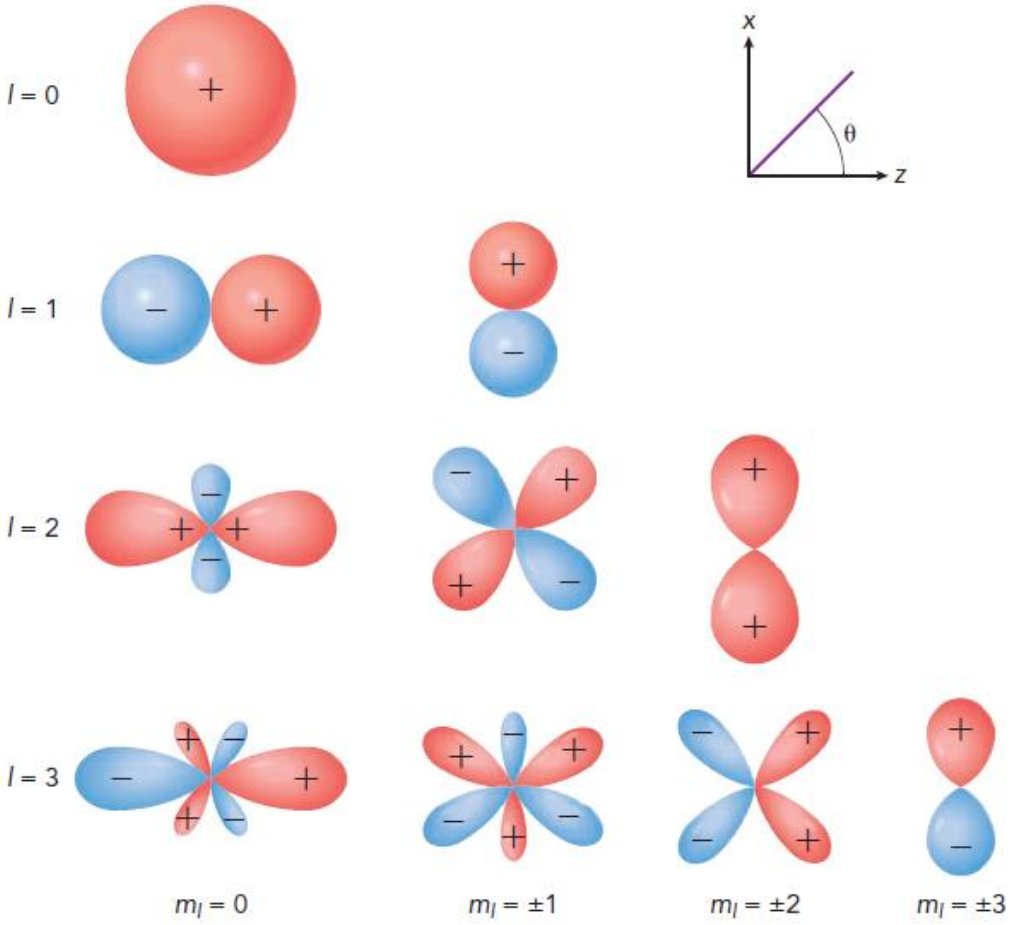


Figure 6: The θ-dependent term of the angular wavefunctions for the electron in a one-electron atom. These are cross-sections taken of the angular wavefunction in the *xz* plane.

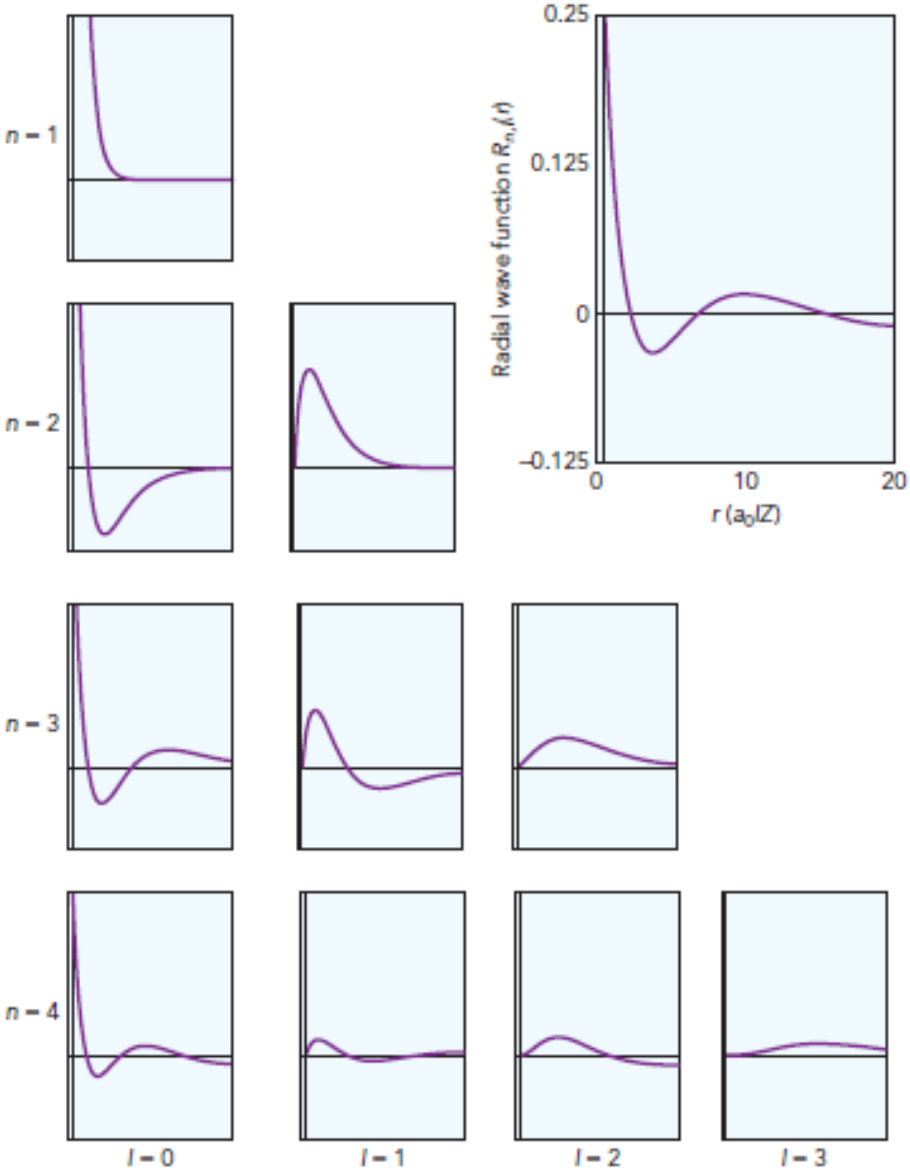
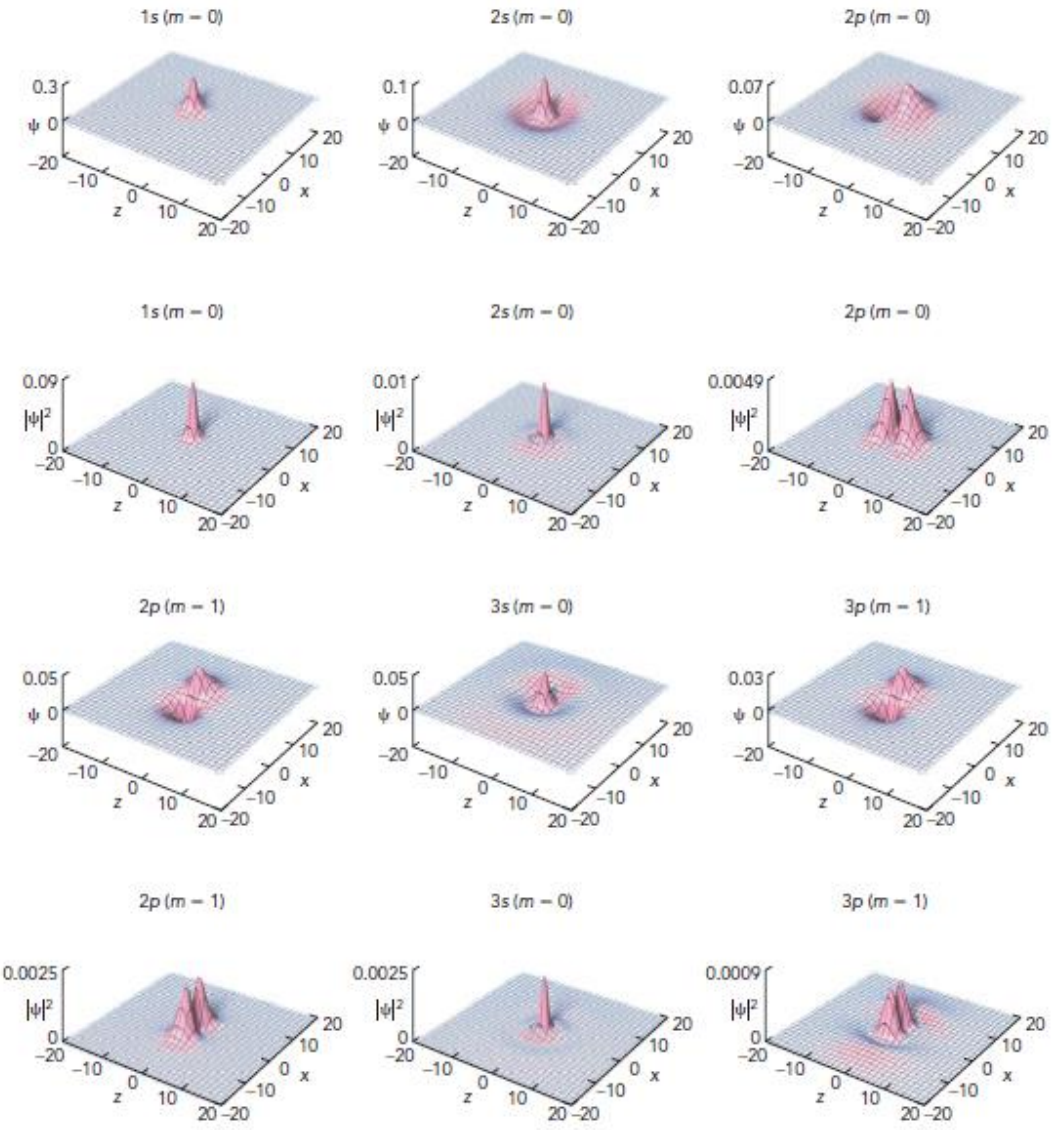


Figure 7: The radial wavefunctions $R_{n,l}(r)$ for the electron in a one-electron atom. The inset in the upper right corner gives the vertical scale in units of $\left(\frac{a_0}{Z}\right)^{-3/2}$ and horizontal scale in $\frac{a_0}{Z}$.


1s (m = 0)
2s (m = 0)
2p (m = 0)
1s (m = 0)
2s (m = 0)
2p (m = 0)
2p (m = 1)
3s (m = 0)
3p (m = 1)
2p (m = 1)
3s (m = 0)
3p (m = 1)
ψ
|ψ|²
x
z

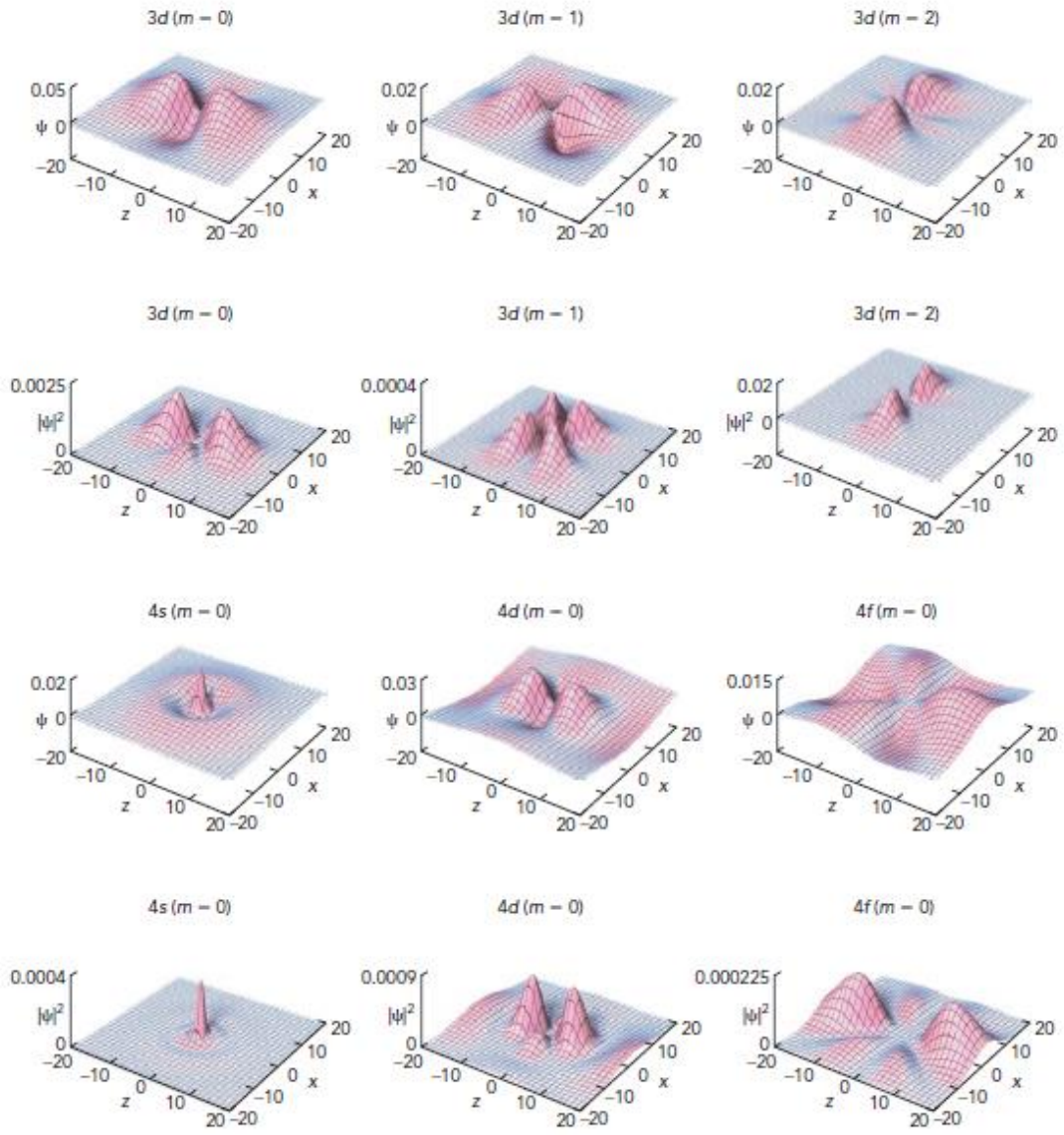


Figure 8: Cross-sections in the *xz* plane of the wavefunctions and probability densities for selected one-electron orbitals. Only the real part of the wavefunction is graphed. Axis values are in atomic units (a_0 for *x* and *z*, $a_0^{-3/2}$ for ψ, a_0^{-3} for $|\psi|^2$). The horizontal axes are of equal scale in all graphs, but the vertical axes are adjusted for clarity.

The analysis of the eigenvalues and eigenfunctions of the Schrodinger equation for the hydrogen atom

1. *What does the energy equation tells us?*

Solving the Schrödinger equation for the hydrogen atom was difficult, but Schrödinger himself achieved it in 1927. He found that the allowed energy levels for an electron in a hydrogen atom are:

$$E_n = -\frac{hR}{n^2} \qquad R = \frac{m_e e^4}{8h^3\varepsilon_0^2}$$

These energy levels have exactly the form suggested spectroscopically, but now we also have an expression for *R* in terms of more fundamental constants.

A very similar expression applies to other one-electron ions, such as He^+ or C^{5+}, with atomic number Z:

$$E_n = -\frac{Z^2 hR}{n^2}, n = 1,2,3, \ldots$$

Z: atomic number

h: Planck's constant

n: principal quantum number

R: Rydberg constant = 3.29×10^{15} Hz

It is clear from the energy equation that:

1. All the energies are negative, meaning that the electron has a lower energy in the atom than when it is far from the nucleus. Because *Z* appears in the numerator, we see that the greater the value of the nuclear charge the more tightly the electron is bound to a nucleus. That *n* appears in the denominator shows that as n increases, the energy becomes less negative.
2. The dependence of the energy on Z^2 rather than on *Z* itself arises from two factors: first, a nucleus of atomic number *Z* and charge *Ze* gives rise to a field that is *Z* times stronger than that of a single proton; second, the electron is drawn in by the higher charge and is *Z* times closer to the nucleus than it is in hydrogen.

Figure (9) shows the energy levels calculated from Energy equation. We see that they come closer together as *n* increases.

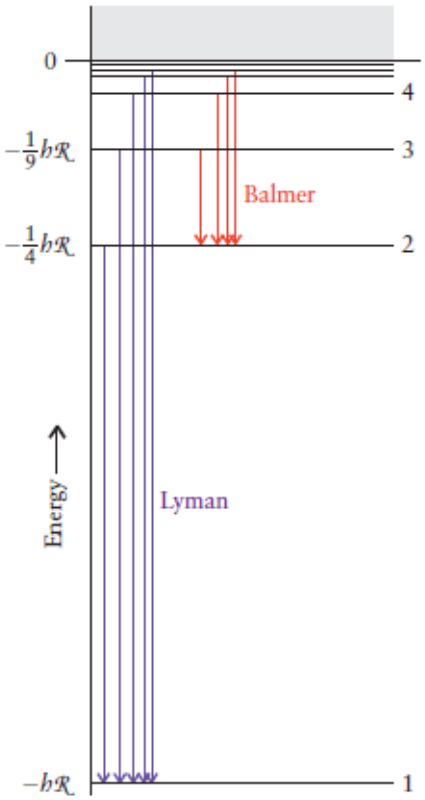


Figure 9: The permitted energy levels of a hydrogen atom. The levels are labeled with the quantum number *n*, which ranges from 1 (for the lowest state) to infinity (for the separated proton and electron).

Each level is labeled by the integer *n*, which is called the ***principal quantum number***, from *n* = 1 for the first (lowest, most negative) level, *n* = 2 for the second, continuing to infinity. The lowest energy possible for an electron in a hydrogen atom, *hR* , is obtained when *n* = 1. This lowest energy state is called the ground state of the atom. A hydrogen atom is normally found in its ground state, with its electron in the level with *n* = 1. When the bound electron is excited by absorbing a photon, its energy climbs up the ladder of levels as *n* increases. It reaches the top of the ladder, corresponding to *E* = 0 and freedom, when *n* reaches infinity. At that point, the electron has left the atom. This process is called ***ionization***. The difference in energy between the ground state and the ionized state is the energy required to remove an electron from the neutral atom in its ground state. The "ionization energy" itself, is the minimum energy needed to achieve ionization, with the electron removed from the orbital with *n* = 1 to a final state in which it has zero energy: in this final state it is free of the nucleus and has zero kinetic energy.

2. What does the wavefunction equation tells us?

Atomic orbitals:

Knowing the form of the wavefunctions allows us to know how the electron is distributed around the nucleus.

The wavefunctions of electrons in atoms are called atomic orbitals. The name was chosen to suggest something less definite than an "orbit" of an electron around a nucleus and to take into account the wave nature of the electron. Moreover, we must never lose sight of their interpretation, that the square of a wavefunction tells us the probability density of an electron at each point. To visualize this probability density, imagine a cloud centered on the nucleus. The density of the cloud at each point represents the probability of finding an electron there. Denser regions of the cloud therefore represent locations where the electron is more likely to be found.

Each wavefunction, which in general varies from point to point, can be written as a function of the coordinates, $\psi(r,\theta,\phi)$. It turns out, however, that all the wavefunctions can be written as the product of a function that depends only on r and another function that depends only on the angles θ and ϕ. That is,

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

The function $R(r)$ is called the ***radial wavefunction***; it tells us how the wavefunction varies as we move away from the nucleus in any direction. The function $Y(\theta,\phi)$ is called the ***angular wavefunction***; it tells us how the wavefunction varies as the angles θ and ϕ change.

For example, the wavefunction corresponding to the ground state of the hydrogen atom (n =1) is

$$\psi(r,\theta,\phi) = \frac{\overbrace{2e^{-r/a_0}}^{R(r)}}{a_0^{3/2}} \times \frac{\overbrace{1}^{Y(\theta,\phi)}}{2\pi^{1/2}} = \frac{e^{-r/a_0}}{(\pi a_0^3)^{1/2}} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

The quantity a_0 is called the Bohr radius; when the values of the fundamental constants are inserted, we find a_0 = 52.9 pm.

What does this equation tell us?

1. For this wavefunction, the angular wavefunction Y is a constant, $\frac{1}{2\sqrt{\pi}}$, independent of the angles, which means that the wavefunction is the same in all directions. The radial wavefunction $R(r)$ decays exponentially toward zero as r increases, which means that the probability density is highest close to the nucleus ($e^0 = 1$). The Bohr radius tells us how sharply the wavefunction falls away with distance: when $r = a_0$, ψ has fallen to 1/e (37%) of its value at the nucleus.
2. All the higher energy levels have more than one wavefunction for each energy level. One of the wavefunctions for the next higher energy level, with $n = 2$ and $E_2 = -\frac{1}{4}hR$, is

$$\psi(r,\theta,\phi) = \overbrace{\frac{1}{2\sqrt{6}}\frac{1}{a_0^{5/2}}\, r\, e^{-r/2a_0}}^{R(r)} \times \overbrace{\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi}^{Y(\theta,\phi)}$$

$$= \frac{1}{4}\left(\frac{1}{4\pi a_0^5}\right)^{1/2} \boldsymbol{r} e^{-r/2a_0} \sin\theta\cos\phi$$

What does this equation tell us?

This wavefunction also falls exponentially toward zero as r increases. Notice, though, that the exponential function is multiplied by the factor r, so ψ is zero at the nucleus (at $r = 0$) as well as far away from it.

The expressions for a number of other atomic orbitals are shown in Table (1). To understand these tables, we need to know that each wavefunction is labeled by three quantum numbers: ***n*** is *related to the size and energy of the orbital*, ***l*** *is related to its shape*, and $\boldsymbol{m_l}$ *is related to its orientation in space*.

When the Schrödinger equation is solved in detail, it turns out that three quantum numbers are needed to label each wavefunction (because the atom is three-dimensional). The three quantum numbers are designated n, l, and m_l. More surprisingly, it also turns out that, for a hydrogen atom, wavefunctions with the same value of n all have the same energy regardless of the values of the other two quantum numbers.

Interpretation of the Quantum Numbers

The solution of Schrödinger equation for the hydrogen atoms introduced three quantum numbers to label each wavefunction. These quantum numbers are convenient numerical labels for quantum states, often related to the index of a sum, or the exponent in a power series, or both. In any quantum system, distinct quantum numbers are used for each degree of freedom, each coordinate into which energy can be channeled. The three quantum numbers are designated n, l, and m_l. Each quantum number is a unitless number, and the higher its value, the more energy there is in the motion along its corresponding degree of freedom. We have three degrees of freedom in the one-electron atom- r, θ, and ϕ- and three quantum numbers:

1. **The principal quantum number, (n)**

It determines the total number of nodes (equal to n - 1) in the real part of the wave function, and the corresponding energy of the state (The value of n can be used to calculate the energy of an electron) as well as it is related to the size of the orbital. We can associate n roughly with the coordinate r because increases in the energy cause the electron to move further from the nucleus on average, regardless of any change in the angular motion. We shall call the group of quantum states that share the same value of n the n^{th} shell. All atomic orbitals with the same value of the principal quantum number n have the same energy and are said to belong to the same shell of the atom. The name "shell" reflects the fact that as n increases, the region of greatest probability density is like a nearly hollow shell of increasing radius. The higher the number of the shell, the further away from the nucleus are the electrons in that shell.

2. **The orbital angular momentum (azimuthal) quantum number (l)**

This quantum number can take the values: l=0, 1, 2, …, n-1.

There are n different values of l for a given value of n. For instance, when n = 4, l can have any of the three values 0, 1, 2, and 3. The orbitals of a shell with principal quantum number n therefore fall into n **subshells**, groups of orbitals that have the same value of l (i.e., the subshell is group of quantum states that share the same values of both n and l). There is only one subshell in the n = 1 level (l = 0), two in the n = 2 level (l = 0 and 1), three in the n = 3 level (l = 0, 1, and 2), and so on. All orbitals with l = 0 are called s-orbitals, those with l = 1 are called p-orbitals, those with l = 2 are called d-orbitals, and those with l =3 are called f-orbitals:

Value of *l*	0	1	2	3
Orbital type	*s*	*p*	*d*	*f*

These labels (s, p, d, and f) come from spectroscopy where lines were classified as sharp, principal, diffuse, and fundamental.

Although higher values of *l* (corresponding to *g*-, *h*-, . . . orbitals) are possible, the lower values of *l* (0, 1, 2, and 3) are the only ones that chemists need in practice.

The value of *l* can be used to calculate the physical property; the orbital angular momentum of the electron, a measure of the rate at which (in classical terms) the electron "circulates" round the nucleus, i.e., it distinguishes among states with different orbital angular momenta, as given by the eigenvalue $\hbar^2 l(l+1)$ of $\hat{L}^2$:

Orbital angular momentum= $\left(\sqrt{l(l+1)}\right)\hbar$

Because it describes the overall orbital angular momentum, *l* is associated with excitation along both θ and ϕ.

An electron in an *s*-orbital (an "*s*-electron"), for which *l* = 0, has zero orbital angular momentum. That means that we should imagine it not as circulating around the nucleus but simply as distributed evenly around it. An electron in a *p*-orbital (*l* =1) has nonzero orbital angular momentum (of magnitude $\left(\sqrt{2}\right)\hbar$; so it can be thought of as circulating around the nucleus. An electron in a *d*-orbital (*l*=2) has a higher orbital angular momentum $\left(\sqrt{6}\right)\hbar$, one in an f-orbital (*l* = 3) has an even higher angular momentum $\left(\sqrt{12}\right)\hbar$, and so on.

As mentioned before, for the hydrogen atom, all the orbitals of a given shell have the same energy, regardless of the value of their orbital angular momentum (simply because *l* does not appear in the energy expression). We say that the orbitals of a shell in a hydrogen atom are degenerate. This degeneracy is true only of the hydrogen atom and one-electron ions (such as He^+ and C^{5+}).

3. The magnetic quantum number, (m_l):

It distinguishes the individual orbitals within a subshell (i.e., distinguishes among wavefunctions with the same angular momentum but different projections of the angular momentum onto the *z* axis. This quantum number can take the values

$m_l = l, l\text{-}1, \ldots, -l$

There are $2l + 1$ different values of m_l for a given value of l and therefore $2l + 1$ orbitals in a subshell of quantum number l. For example, when l=1, m_l = +1, 0, -1; so there are three *p*-orbitals in a given shell. Alternatively, we can say that a subshell with l=1 consists of three orbitals.

We showed in Eq. 3.12 that the eigenvalue of the operator $\hat{L}_z$ is $\hbar m_l$. Because L_z is determined by the motion along ϕ, the ϕ -dependent part of the wavefunction determines the value of m_l. The state that corresponds to a particular value of n, l, and m_l will be called an atomic orbital.

The magnetic quantum number tells us the orientation of the orbital motion of the electron. Specifically, it tells us that the orbital angular momentum around an arbitrary axis is equal to $\hbar m_l$, the rest of the orbital motion (to make up the full amount of $\left(\sqrt{l(l+1)}\right)\hbar$) being around other axes. For instance, if m_l =+1, then the orbital angular momentum of the electron around the arbitrary axis is $+\hbar$, whereas, if m_l= ⁻1, then the orbital angular momentum of the electron around the same arbitrary axis is $-\hbar$. The difference in sign simply means that the direction of motion is opposite, the electron in one state circulating clockwise and an electron in the other state circulating counterclockwise. If m_l =0, then the electron is not circulating around the selected axis, but rather is evenly distributed around it.

The hierarchy of shells, subshells, and orbitals is summarized in Fig. 1.30 and Table 1.3. Each possible combination of the three quantum numbers specifies an individual orbital. For example, an electron in the ground state of a hydrogen atom has the specification n =1, l = 0, ml = 0. Because l = 0, the ground-state wavefunction is an example of an *s*-orbital and is denoted 1*s*. Each shell has one *s*-orbital, and the *s*-orbital in the shell with quantum number n is called an *ns*-orbital.

In other words, If we want to specify the subshell, we will write the n value and the symbol for the l value; for example, the 3*d* subshell has n = 3 and l = 2. For convenience, we will add the m_l value as a subscript if we want to specify the exact orbital in the subshell (e.g., $3d_{-1}$ indicates the m_l = -1 orbital of the 3*d* subshell), but this is not a standard notation.

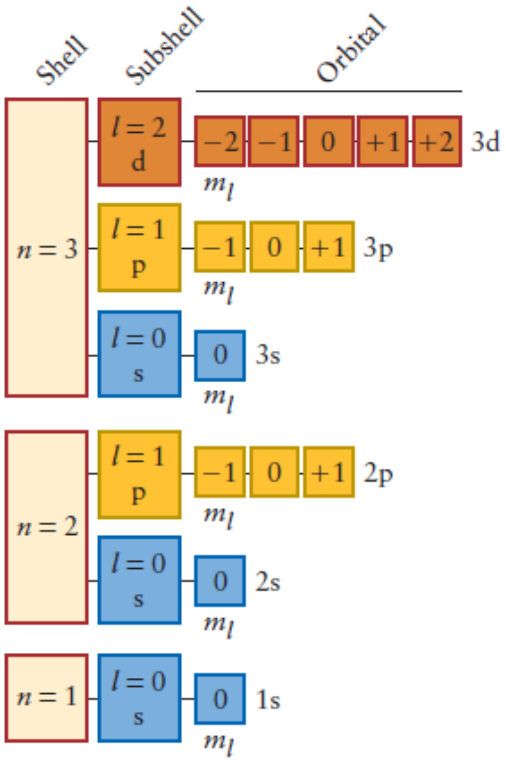


Figure 1: A summary of the arrangement of shells, subshells, and orbitals in an atom and the corresponding quantum numbers. Note that the quantum number m_l is an alternative label for the individual orbitals: in chemistry, it is more common to use *x*, *y*, and *z* instead.

Table 1: Quantum Numbers for electrons in atoms:

Name	Symbol	Values	Specifies	indicates
principal	n	1, 2,3, …	shell	Size
orbital angular momentum	l	0, 1, …, n-1	subshell: l = 0, 1, 2, 3, 4,… s, p, d, f, g, …	shape
magnetic	m_l	l, l-1, …, -l	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}$, $-\frac{1}{2}$	spin state	spin direction

4. Spin quantum number m_s:

According to quantum mechanics, an electron has two spin states, represented by the arrows ↑ (up) and ↓ (down) or the Greek letters α (alpha) and β (beta).We can think of an electron as being able to spin counterclockwise at a certain rate (the ↑ state) or clockwise at exactly the same rate (the ↓ state). These two spin states are distinguished by a fourth quantum number, the spin magnetic quantum number, m_s. This quantum number can have only two values: $+\frac{1}{2}$ indicates an ↑ electron and $-\frac{1}{2}$ indicates a ↓ electron (Fig. 2).

↑ $m_s = +\frac{1}{2}$ ↓ $m_s = -\frac{1}{2}$

Figure 2: The two spin states of an electron can be represented as clockwise or counterclockwise rotation around an axis passing through the electron. The two states are identified by the quantum number ms and depicted by the arrows shown on the right.

The electron is in the lowest energy level, the ground state of the atom, with $n = 1$. The only orbital with this energy is the 1*s*-orbital; we say that the electron occupies a 1*s*-orbital or that it is a "1*s*-electron." The electron in the ground state of a hydrogen atom is described by the following values of the four quantum numbers: $n = 1$ $l = 0$ $m_l = 0$ $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$.

The electron can have either spin state.

When the atom acquires enough energy (by absorbing a photon of radiation, for instance) for its electron to reach the shell with $n = 2$, it can occupy any of the four orbitals in that shell. There are one 2*s*- and three 2*p*-orbitals in this shell; in hydrogen, they all have the same energy. When an electron is described by one of these wavefunctions, we say that it "occupies a 2*s*-orbital" or one of the 2*p*-orbitals or that it is "a 2*s*or 2*p*-electron." The average distance of an electron from the nucleus when it occupies any of the orbitals in the shell with $n = 2$ is greater than when $n = 1$, and so we can think of the atom as swelling up as it is excited energetically. When the atom acquires even more energy, the electron moves into the shell with $n = 3$; the atom is now even larger. In this shell, the electron can occupy any of nine orbitals (one 3*s*-, three 3*p*-, and five 3*d*-orbitals). More energy moves the electron still farther from the nucleus to the $n = 4$ shell, where sixteen orbitals are available (one 4*s*-, three 4*p*-, five 4*d*-, and seven 4*f*-orbitals). Eventually, enough energy is absorbed so that the electron can escape the pull of the nucleus and leaves the atom.

Electron Spin

In 1921, the American physicist Arthur H. Compton, who was studying the scattering of X rays from crystal surfaces, conclude that "the electron itself, spinning like a tiny gyroscope, is probably the ultimate magnetic particle." In 1922, two German physicists, Otto Stern and Walther Gerlach, passed a beam of silver atoms ($4d^{10}5s^{1}$), through an inhomogeneous magnetic field in order to split the beam into its $2l + 1$ space-quantized components. A homogeneous magnetic field will orient magnetic dipoles but not exert a translational force. An inhomogeneous magnetic field, however, will exert a translational force and hence spatially separate magnetic dipoles that are oriented differently. Classically, a beam of magnetic dipoles will orient themselves through a continuous angle and so will become spread out in a continuous manner.

Quantum-mechanically, however, a state with a given value of l will be restricted to $2l + 1$ discrete orientations, and so such a system will be split into $2l + 1$ components by an inhomogeneous magnetic field. Stern and Gerlach found the quite unexpected result that a beam of silver atoms splits into only two parts. Note that this corresponds to $2l + 1 = 2$, or to $l = 1/2$. Up to now we have admitted only integer values of l.

Another similar observation is the splitting that occurs in atomic spectra. For example, under high resolution it was observed that the $n = 2$ to $n = 1$ transition in atomic hydrogen is split into two closely spaced lines, called a *doublet.*

In 1925, **Wolfgang Pauli** showed that all these observations could be explained with the postulate that an electron can exist in two distinct states. For this purpose, Pauli introduced a fourth quantum number which now called the *spin quantum number* m_s, that is restricted to the two values $+\frac{1}{2}$ and $-\frac{1}{2}$. It is interesting that Pauli did not give any interpretation to this fourth quantum number. The existence of a fourth quantum number was somewhat of a mystery because the three spatial coordinates of an electron account for n, l, and m_l, but what is this quantum number due to?

It was finally two young Dutch physicists, George Uhlenbeck and Samuel Goudsmit, in 1925, who showed that the two intrinsic states of an electron could be identified with two angular momenta, or spin, states. We have seen earlier that the orbital motion of electrons leads to an associated magnetic moment.

In 1928, the British physicist Paul Dirac developed a relativistic extension of the quantum mechanics of an electron, and in his treatment electron spin arises naturally. In the nonrelativistic quantum mechanics to which we are confining ourselves, electron spin must be

introduced as an additional hypothesis. We have learned that each physical property has its corresponding linear Hermitian operator in quantum mechanics. **The spin angular momentum** of a microscopic particle has no analog in classical mechanics, and so, we cannot construct operators for spin as usual. To do this, we shall simply use symbols for the spin operators, without giving an explicit form for them.

Analogous to the orbital angular-momentum operators $\hat{L}^2, \hat{L}_x, \hat{L}_y, \hat{L}_z$, we have the spin angular-momentum operators $\hat{S}^2, \hat{S}_x, \hat{S}_y, \hat{S}_z$, which are postulated to be linear and Hermitian. $\hat{S}^2$ is the operator for the square of the magnitude of the total spin angular momentum of a particle. $\hat{S}_z$ is the operator for the z component of the particle's spin angular momentum. We have:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

The **eigenvalues** of $\hat{S}^2$ are

$$s(s+1)\hbar^2, \qquad s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \tag{19}$$

and the **eigenvalues** of $\hat{S}_z$ are

$$m_s\hbar, \qquad m_s = -s, -s+1, \ldots, s-1, s \tag{20}$$

The quantum number ***s*** is called the **spin** of the particle.

With $s = \frac{1}{2}$, the magnitude of the total spin angular momentum of an electron is given by the square root of (19) as

$$\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2} = \sqrt{\frac{1}{2}\left(\frac{3}{2}\right)\hbar^2} = \sqrt{\left(\frac{3}{4}\right)\hbar^2} = \frac{1}{2}\left(\sqrt{3}\right)\hbar$$

For $s = \frac{1}{2}$, Eq. (20) gives the possible eigenvalues of $\hat{S}_z$ of an electron as $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. The electron spin eigenfunctions that correspond to these $\hat{S}_z$ eigenvalues are denoted by α and β:

$$\hat{S}_z\alpha = +\frac{1}{2}\hbar\alpha$$

$$\hat{S}_z\beta = +\frac{1}{2}\hbar\beta$$

The terms *spin up* and *spin down* refer to $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$, respectively. See **Fig. 3**. We shall later show that the two possibilities for the quantum number m_s give the doubling of lines in the spectra of the alkali metals.

Figure 3: Possible orientations of the electron spin vector with respect to the *z* axis. In each case, **S** lies on the surface of a cone whose axis is the *z* axis.

Spin and the Hydrogen Atom

The wave function specifying the state of an electron depends on the coordinates *x*, *y*, and *z* and also on the spin state of the electron. What effect does this have on the wave functions and energy levels of the hydrogen atom? To a very good approximation, the Hamiltonian operator for a system of electrons does not involve the spin variables but is a function only of spatial coordinates and derivatives with respect to spatial coordinates. As a result, we can separate the stationary-state wave function of a single electron into a product of space and spin parts:

$$\psi(x,y,z)g(m_s)$$

where g(m_s) is either one of the functions α or β, depending on whether $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$. [More generally, g(m_s) might be a linear combination of α and β; g(m_s) = $c_1\alpha + c_2\beta$.]

Since the Hamiltonian operator has no effect on the spin function, we have

$$\hat{H}[\psi(x,y,z)g(m_s)] = g(m_s)\hat{H}\psi(x,y,z) = E[\psi(x,y,z)g(m_s)]$$

and we get the same energies as previously found without taking spin into account. The only difference spin makes is to double the possible number of states. Instead of the state $\psi(x,y,z)$, we have the two possible states $\psi(x,y,z)\alpha$ and $\psi(x,y,z)\beta$. When we take spin into account, the degeneracy of the hydrogen-atom energy levels is $2n^2$ rather than n^2.

The Spin–Statistics Theorem (*many-electron systems not Hydrogen***)**

Suppose we have a system of several identical particles. In classical mechanics the identity of the particles leads to no special consequences. For example, consider identical billiard balls rolling on a billiard table. We can follow the motion of any individual ball, say by taking a motion picture of the system. We can say that ball number one is moving along a certain path, ball two is on another definite path, and so on, the paths being determined by Newton's laws of motion. Thus, although the balls are identical, we can distinguish among them by specifying the path each takes. The identity of the balls has no special effect on their motions. In quantum mechanics the uncertainty principle tells us that we cannot follow the exact path taken by a microscopic "particle." If the microscopic particles of the system all have different masses or charges or spins, we can use one of these properties to distinguish the particles from one another. But if they are all identical, then the one way we had in classical mechanics of distinguishing them, namely by specifying their paths, is lost in quantum mechanics because of the uncertainty principle. Therefore, **the wave function of a system of interacting identical particles must not distinguish among the particles**. For example, in the treatment of the helium-atom excited states, the function $1s(1)2s(2)$, which says that electron 1 is in the 1*s* orbital and electron 2 is in the 2*s* orbital, is not a correct wave function.

Rather, we had to use the functions $\frac{1}{\sqrt{2}}[1s(1)2s(2) \pm 1s(2)2s(1)]$, which do not specify which electron is in which orbital. (If the identical particles are well separated from one another so that their wave functions do not overlap, they may be regarded as distinguishable.)

We now derive the restrictions on the wave function due to the requirement of indistinguishability of identical particles in quantum mechanics. The wave function of a system of *n* identical microscopic particles depends on the space and spin variables of the particles. For particle 1, these variables are x_1, y_1, z_1, m_{s1}. Let q_1 stand for all four of these variables. Thus $\psi = \psi(q_1, q_2, \dots, q_n)$.

As we have seen in postulate (III), when we discussed the exchange (or permutation) operator $\hat{\boldsymbol{P}}_{\mathbf{12}}$ that interchanges all the coordinates of particles 1 and 2: $\hat{P}_{12} f(q_1, q_2, q_3, \dots, q_n) = f(q_2, q_1, q_3, \dots, q_n)$, the eigenvalues of $\hat{P}_{12}$ are + 1 and -1. And the eigenfunction may be either ***symmetric*** (with respect to interchange of particles 1 and 2) ***with eigenvalue +1***,or ***antisymmetric*** (with respect to interchange of particles 1 and 2) ***with eigenvalue -1.***

The operator $\hat{P}_{ik}$ is defined by:

$$\hat{P}_{ik} f(q_1, \dots, q_i, \dots, q_k, \dots, q_n) = f(q_1, \dots, q_k, \dots, q_i, \dots, q_n)$$

The eigenvalues of $\hat{P}_{ik}$ are, like those of $\hat{P}_{12}$, +1 and -1.

We now consider the wave function of a system of *n* identical microscopic particles. Since the particles are indistinguishable, the way we label them cannot affect the state of the system. Thus the two wave functions

$\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n)$ and $\psi(q_1, \dots, q_k, \dots, q_i, \dots, q_n)$

must correspond to the same state of the system. Two wave functions that correspond to the same state can differ at most by a multiplicative constant. Hence

$$\psi(q_1, \dots, q_k, \dots, q_i, \dots, q_n) = c\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n)$$

$$\hat{P}_{ik}\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n) = c\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n)$$

The last equation states that ψ is an eigenfunction of $\hat{P}_{ik}$. But we know that the only possible eigenvalues of $\hat{P}_{ik}$ are 1 and -1. We conclude that the wave function for a system of *n* identical particles must be symmetric or antisymmetric with respect to interchange of any two of the identical particles, *i* and *k*. Since the *n* particles are all identical, we could not have the wave function symmetric with respect to some interchanges and antisymmetric with respect to other interchanges. Thus the wave function of *n* identical particles must be either symmetric with respect to every possible interchange or antisymmetric with respect to every possible interchange of two particles. (**The argument just given is not rigorous. The statement that the wave function of a system of identical particles must be either completely symmetric or completely antisymmetric with respect to interchange of two particles is called the *symmetrization postulate***.)

We have seen that there are two possible cases for the wave function of a system of identical particles, the symmetric and the antisymmetric cases. **Experimental evidence** (such as the periodic table of the elements) shows that **for electrons only** the antisymmetric case occurs. Thus we have an additional postulate of quantum mechanics, which states that *the wave function of a system of electrons must be antisymmetric with respect to interchange of any two electrons*.

Dirac concluded (based on theoretical work and experimental data) that electrons require antisymmetric wave functions and photons require symmetric wave functions. However, Dirac and other physicists erroneously believed in 1926 that all material particles required antisymmetric wave functions. In 1930, **experimental data** indicated that a **particles** (which have $s = 0$) require symmetric wave functions; **physicists eventually realized that what determines whether a system of identical particles requires symmetric or antisymmetric wave functions is the spin of the particle**:

1. Particles with half-integral spin ($s = \frac{1}{2}, \frac{3}{2}$ and so on) require antisymmetric wave functions,
2. Particles with integral spin ($s = 0, 1$, and so on) require symmetric wave functions.

In 1940, the physicist **Wolfgang Pauli** used relativistic quantum field theory to prove this result. Particles requiring antisymmetric wave functions, such as electrons, protons and each neutrons, are called **fermions** (after E. Fermi), whereas particles requiring symmetric wave functions, such as pions, are called **bosons** (after S. N. Bose).

In nonrelativistic quantum mechanics, we must postulate that *the wave function of a system of identical particles must be antisymmetric with respect to interchange of any two particles if the particles have half-integral spin and must be symmetric with respect to interchange if the particles have integral spin.* This statement is called the **spin–statistics theorem** (since the statistical mechanics of a system of bosons differs from that of a system of fermions).

The spin–statistics theorem has an important consequence for a system of identical fermions. The antisymmetry requirement means that

$$\psi(q_1, q_2, q_3, \dots, q_n) = -\psi(q_2, q_1, q_3, \dots, q_n) \qquad (17)$$

Consider the value of ψ when electrons 1 and 2 have the same coordinates, that is, when $x_1 = x_2$, $y_1 = y_2$, $z_1 = z_2$, and $m_{s1} = m_{s2}$. Putting $q_2 = q_1$ in (17), we have:

$$\psi(q_1, q_1, q_3, \dots, q_n) = -\psi(q_1, q_1, q_3, \dots, q_n)$$

$$2\psi = 0$$

$$\psi(q_1, q_1, q_3, \dots, q_n) = 0 \qquad (18)$$

Thus, two electrons with the same spin have zero probability of being found at the same point in three-dimensional space. (By "the same spin," we mean the same value of m_s). Since ψ is a continuous function, Eq. (18) means that the probability of finding two electrons with the same spin close to each other in space is quite small. Thus the antisymmetry requirement forces electrons of like spin to keep apart from one another. To describe this, one often speaks of a **Pauli repulsion** between such electrons. This "repulsion" is not a real physical force, but a reflection of the fact that the electronic wave function must be antisymmetric with respect to exchange.

The requirement for symmetric or antisymmetric wave functions also applies to a system containing two or more identical composite particles. Consider, for example, an $^{16}O_2$

molecule. The ^{16}O nucleus has 8 protons and 8 neutrons. Each proton and each neutron has s = $\frac{1}{2}$ and is a fermion. Therefore, interchange of the two ^{16}O nuclei interchanges 16 fermions and must multiply the molecular wave function by $(-1)^{16} = 1$. Thus the $^{16}O_2$ molecular wave function must be symmetric with respect to interchange of the nuclear coordinates. **The requirement for symmetry or antisymmetry with respect to interchange of identical nuclei affects the degeneracy of molecular wave functions and leads to the symmetry number in the rotational partition function**.

For interchange of two identical composite particles containing *m* identical bosons and *n* identical fermions, the wave function is multiplied by $(+1)^m(-1)^n = (-1)^n$.

A composite particle is thus a fermion if it contains an odd number of fermions and is a boson otherwise.